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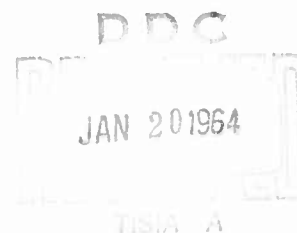
## INVESTIGATION OF ELASTIC AND THERMAL PROPERTIES OF CARBON-BASE BODIES

TECHNICAL REPORT NO. WADC-TR-58-360, PART V

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## FOREWORD

This report was prepared by the Carbon Research Laboratory at the State University of New York at Buffalo, Buffalo, New York, under USAF Contract No. AF 33(616)-7791. This contract was initiated under Project No. 7350 "Refractory Inorganic Nonmetallic Materials," Task No. 735002 "Refractory Inorganic Non-metallic Materials: Graphitic." The work was administered under the direction of the A. F. Materials Laboratory Research and Technology Division, with Mr. C. A. Pratt as project engineer.

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## ABSTRACT

In continuation of the work on elastic properties of carbons, using the greatly improved high temperature equipment, families of curves of the dependence of Young's modulus on temperature and on the heat treatment have been obtained for four basic types of carbons and as far as possible, for a number of special types of commercial carbons. The amplitude dependence of internal friction and dynamic Young's modulus were investigated in the sonic range for a number of types of carbons as made and also neutron irradiated, as well as the temperature dependence of internal friction of the resonance frequency from room down to liquid hydrogen temperature. The presence of a Bordoni peak at 50°K has been found connected with the relaxation of motion of dislocations. Families of curves of the dependence of heat conductivity and electric resistivity on temperature and on the heat treatment have been obtained for four basic types of carbons, using an improved technique. The "steady" sinusoidal wave technique for determination of heat diffusivity has been improved in precision and extended in temperature range and data collected for several types of graphitized materials.

This technical report has been reviewed and is approved.



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## I. INTRODUCTION

The aim of this project was to study elastic properties of carbons and graphites and to investigate the heat conduction and heat diffusivity of graphite in a wide range of temperatures in relation to the main fabrication variables and to the basic types of carbons tested. With the exception of the mechanical strength, all the factors affecting the resistance of the carbon materials to temperature shocks were subjected to testing in our laboratory. In the previous Technical Reports, Part I<sup>1</sup>, Part II<sup>2</sup>, Part III<sup>3</sup> and Part IV<sup>4</sup> the results of the previous work up to January 1962 were described. This included a number of research projects; first the construction of a novel high precision equipment for studies of deformation at room temperature. With this equipment broad studies of the creep and permanent set, as well as of the elastic moduli E and G in relation to the type of carbon material and its heat-treatment temperature were carried out. Later this equipment was improved and some more data collected. Some studies of Poisson ratio were made. The four basic types of carbon investigated were made of: 1) soft filler-soft binder, 2) soft filler-hard binder, 3) hard filler-soft binder and 4) hard filler-hard binder. In addition to these, carbons made using graphitized filler (soft and hard) as well as impregnated carbons and graphites, were investigated. The experience gained in operation of the room temperature equipment permitted the successful construction of the high temperature elasticity apparatus, of a completely novel design and of a very high sensitivity and precision. The results obtained for the four basic types graphite rods were reported in form of force deflection loops and of curves of dependence of elastic modulus on temperature up to 2200°C. It was found that only carbons made with soft filler show maxima at high temperature. Also for the first time complete families of curves were obtained for the dependence of Young's modulus on temperature and heat treatment for soft and hard carbons, and the presence of maxima in modulus was found to have a quite general occurrence. It has been found however, that the operation of the equipment presents some difficulties as far as obtaining the more precise shape of these curves is concerned and for that end the electronics associated with this equipment has been rebuilt, just at the end of the previous report period.

Some studies of ultrasonic attenuation in relation to the porosity of the carbons and frequency of vibrations used were carried out. They led to a clarification of the scattering mechanism in carbons and of the nature of the true attenuation being caused by elastic hysteresis. Since the attenuation is predominantly caused by scattering due to the inhomogeneous structure of carbons, in continuation of the work on internal friction, we have limited ourselves to the sonic range of frequencies. For this purpose an apparatus with associated electronics was set up and studies of the dependence of internal friction and of the dynamic Young's modulus on strain amplitude were performed for several types of carbons at room temperature.

A thermal conductivity apparatus for studies in the temperature range 1000° - 3000°C was constructed first of a conventional design and studies of the influence of the environmental atmosphere on the measured conductivities, as well as measurements of the temperature dependence of the conductivity for the four basic types of carbons

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were carried out with this apparatus. Having gained experience with the simplified apparatus, the construction of a new improved conductivity test equipment was carried out, the novel feature of the equipment being its great flexibility, permitting heating of the rod directly by the flow of electric current as well as indirectly by a helical heating coil, or by a combination of both. After the equipment was tested by performing a number of runs which showed its satisfactory operation, and having achieved satisfactory reproducibility, a family of curves for the dependence of the heat conductivity on temperature and heat treatment was obtained for a soft carbon, the system of such curves being for the first time obtained since the unsuccessful attempt was made by Powell and Schofield. Some successful experiments were also performed in trying out a novel arrangement for determination of heat conductivity without internal heat generation and are reported in the same section.

A thermal diffusivity apparatus permitting study of the propagation of periodic sinusoidal heat waves through a carbon was constructed and later improved and measurements of the heat diffusivity carried out in the temperature range  $100^{\circ} - 900^{\circ}\text{C}$ . Charts were prepared using an IBM 1620 computer for a rapid determination of  $\alpha$  from experimental data. Since the extension of this technique to higher temperatures encountered serious difficulties, another apparatus based on a transient heat flow method was constructed and tested in operation in the temperature range  $800^{\circ} - 2800^{\circ}\text{C}$ . The determinations have been considerably improved by the use of a new radiation pyrometer with a much faster response.

In the present report results obtained in continuation of this work are discussed. First, some results of additional work on elastic modulus at room temperature, namely on the dependence of the modulus for a carbon made from raw filler on heat treatment are presented (II). The main effort, however, centered around the studies of the Young's modulus at high temperature (III). With the improved apparatus the following studies were carried out: 1) dependence of Young's modulus on temperature for four basic types of carbons heat treated to  $3000^{\circ}\text{C}$  (soft filler-soft binder, soft filler-hard binder, hard filler-soft binder and hard filler-hard binder), 2) complete systems of temperature dependence curves for these four types of carbons and for glassy carbon (Tokai Electrode Co.) were obtained as these carbons are progressively heat treated to higher temperatures and then cooled back to room temperature, 3) dependence of Young's modulus on temperature was measured for pyrolytic graphite (General Electric Co.) and ZTA graphite (National Carbon Co.). It has been found that for soft filler materials all curves of Young's modulus vs. temperature show a maximum below the heat-treatment temperature. Hard filler bodies show a continuous decrease in modulus with increase of temperature. ZTA and pyrolytic graphite behavior is similar to that of soft filler bodies whereas glassy carbon is similar to hard filler materials.

By means of an electromagnetic driving and detection system investigations of mechanical energy losses under alternating stress have been performed in the sonic range on various carbon solids. Materials studied were a glassy carbon, various baked carbons and polycrystalline graphites and some pyrolytic graphites. It was found that with decreasing strain amplitude the internal friction  $Q^{-1}$  decreases and the dynamic elastic modulus  $E$  increases towards limiting values  $Q_0^{-1}$  and  $E_0$ . Moreover, the amplitude dependent portion of the internal friction  $Q^{-1} - Q_0^{-1}$  is seen to be linearly proportional to the modulus defect  $(E_0 - E)/E_0$  for the same amplitude. A very weak neutron irradiation (dose less than  $10^{14}$  nvt) causes in some cases very large changes in the loss character. These facts can be explained by pinning down dislocations by

point imperfections. The temperature dependence of  $Q_0^{-1}$  for polycrystalline graphite shows a so-called Bordoni peak at 50°K for a frequency of about 12 KC accompanied by a small hump at 80°K. The curve  $E_0$  against temperature shows steep drops in the same ranges of temperature. The Peierls potentials of the glissile dislocations in graphite corresponding to these two peaks are roughly estimated to be 0.07 eV and 0.12 eV respectively.

Using the previously developed and tested equipment in continuation of the work on thermal conductivity and electric resistivity, families of curves for the dependence of these properties on temperature were obtained for variously heat treated samples of carbons of the four basic types, thus supplying a complete heat treatment history for these materials. It has been found that the type for the families of curves for these two properties is mainly determined by the type and graphitizability of the filler materials, similarly as in the case of the elastic modulus.

The "steady" sinusoidal technique used for direct determination of the thermal diffusivity in carbon has been further improved in precision and its temperature range extended to 40° - 1200°C. Measurements of the longitudinal diffusivity were performed, using this technique on various types of carbons graphitized at about 3000°C and the results compared with the transverse diffusivity for the same materials as obtained by using the transient heat technique (800° - 2500°C range). Good correspondence is obtained.

## II. ELASTIC PROPERTIES AT ROOM TEMPERATURE

Elastic modulus of various types of carbons was investigated in our work and the results presented in previous reports. However, one special type of carbon, the so-called raw coke carbon, was not studied. Although it is not an important type of carbon from the practical point of view, its spalling characteristics being unfavorable for production and applications, it is a very interesting type of material since the introduction of binder at an early stage of calcination of the filler prevents the development of high locked-in stresses in the process of baking, both filler and binder shrinking about equally with heat treatment. As a result the material is much stronger and stiffer than the conventional one and exhibits a high thermal expansion due to soaking of filler with the binder<sup>5</sup>. Extrusion of good sound pieces is slightly tricky and requires some practice. Successful extrusions of raw coke mixes were made in form of 1/2 inch diameter rods. The filler material for these mixes was raw Texas coke which had a heat-treatment temperature of about 450°C and the binder was Barrett M-30 coal tar pitch. The mixes contained equal parts by weight of 65/100 and through 200 coke particles. In general, the preparation details were similar to those described in a previous report<sup>1</sup>. Erucic acid was added to the mixes about 3 min. before the end of the mixing cycle (0, 2.5, 5, and 7 percent of the binder by weight) for lubrication purposes. The mixes with 5 and 7 percent erucic acid were easier to extrude than the ones containing 0 and 2.5 percent. Groups of each kind of rods were heat treated to various temperatures to show that they would survive the large gas evolution and dimensional changes occurring during the treatments. Table I gives some results of heat treatments of the raw coke rods. The observed densities are somewhat lower than one usually finds for this type of carbon body.

Table I  
Apparent Density Data for Raw Coke Rods

	ROD NO. 1 (0% ERUCIC ACID)			ROD NO. 2 (2.5% ERUCIC ACID)		
H.T. TEMP. °C	DENSITY gm/cm <sup>3</sup>	WEIGHT GM.	VOLUME CM <sup>3</sup>	DENSITY gm/cm <sup>3</sup>	WEIGHT GM.	VOLUME CM <sup>3</sup>
GREEN	1.34	36.21	27.09	1.30	35.82	27.65
500	1.11	32.03	28.77	1.12	32.03	28.57
750	1.31	29.39	22.41	1.35	30.48	22.54
1000	1.35	29.17	21.54	1.40	30.19	21.51
2800	1.47	28.02	19.06	1.55	28.87	18.67
	ROD NO. 3 (5% ERUCIC ACID)			ROD NO. 4 (7% ERUCIC ACID)		
GREEN	1.31	36.38	27.43	1.32	36.37	27.48
500	1.11	31.65	28.43	1.09	31.08	28.52
750	1.30	29.79	22.95	1.27	29.68	23.46
1000	1.37	29.52	21.57	1.37	29.45	21.49
2800	1.49	28.33	19.02	1.48	28.19	19.06

Young's modulus of such raw soft coke-soft binder rods was investigated as a function of heat-treatment temperature up to 3100°C using the improved room temperature apparatus described in Part IV, p. 4<sup>4</sup>. Heat treatments in the range 500-1000°C were made in the baking oven and higher ones in a graphite tube furnace in an inert atmosphere of nitrogen or argon. Table II gives the results of elasticity measurements on the raw coke rods along with a regular soft filler-soft binder rod for comparison. Rods A and B differ only in the erucic acid content (A - 2.5 percent, B - 5 percent). The important point to notice in Table II is the extremely large shrinkage occurring in the raw coke samples between heat-treatment temperatures of 500° and 1000°C; the raw coke specimens shrink 10 times more than the usual soft filler-soft binder rods! The large shrinkage in the raw coke rods is connected with the evolution of gases from both the coke particles and the binder during the baking process.

Table II

H. T TEMP.	RAW COKE RODS SF-SB						CALCINED COKE SF-SB		
	YOUNG'S MODULUS		VOLUME		DENSITY		E	VOL.	d
	A	B	A	B	A	B			
GREEN	—	—	27.81	27.36	1.29	1.31	—	27.02	1.69
500	3.03	2.92	28.57	29.79	1.12	1.05	8.21	27.43	1.50
750	13.33	13.19	22.35	22.86	1.36	1.30	12.33	26.72	1.52
1000	13.79	13.69	20.42	20.89	1.46	1.40	12.15	26.49	1.52
1200	13.28	12.54	19.95	20.60	1.49	1.41	11.17	26.21	1.50
1400	12.31	11.46	19.26	19.91	1.53	1.45	9.21	26.21	1.50
1600	11.64	11.15	18.75	19.41	1.56	1.48	7.52	25.85	1.50
1800	10.97	10.00	18.74	19.68	1.56	1.45	6.42	26.01	1.48
2000	9.81	8.97	18.74	20.03	1.55	1.42	5.15	26.15	1.46
2200	9.06	8.23	18.75	19.73	1.54	1.44	4.63	25.92	1.47
2400	10.12	8.94	18.56	19.70	1.55	1.43	5.17	25.80	1.47
2600	10.42	9.46	18.46	19.36	1.55	1.46	5.37	25.81	1.47
2800	10.28	9.64	18.23	19.34	1.57	1.46	5.37	25.69	1.48
3100	9.62	9.20	18.38	19.34	1.56	1.46	5.25	25.69	1.48

E    YOUNG'S MODULUS  $10^{10}$  dynes/cm<sup>2</sup>  
 V    VOLUME cm<sup>3</sup>  
 d    DENSITY grams/cm<sup>3</sup>

The heat treatment dependence of the Young's modulus for the raw coke specimens is shown in Fig. 1 along with data from calcined coke soft filler-soft binder and hard filler-hard binder rods. The slope of the E vs. heat-treatment temperature curve for heat-treatment temperatures between 1000° and 2200°C is intermediate between that of soft filler-soft binder and hard filler-hard binder rods. That is to say, raw soft coke filler makes the behavior of E vs. heat-treatment temperature somewhat more like

hard coke fillers. A similar effect was observed several years ago by Collins<sup>5</sup> in studies of thermal expansion.

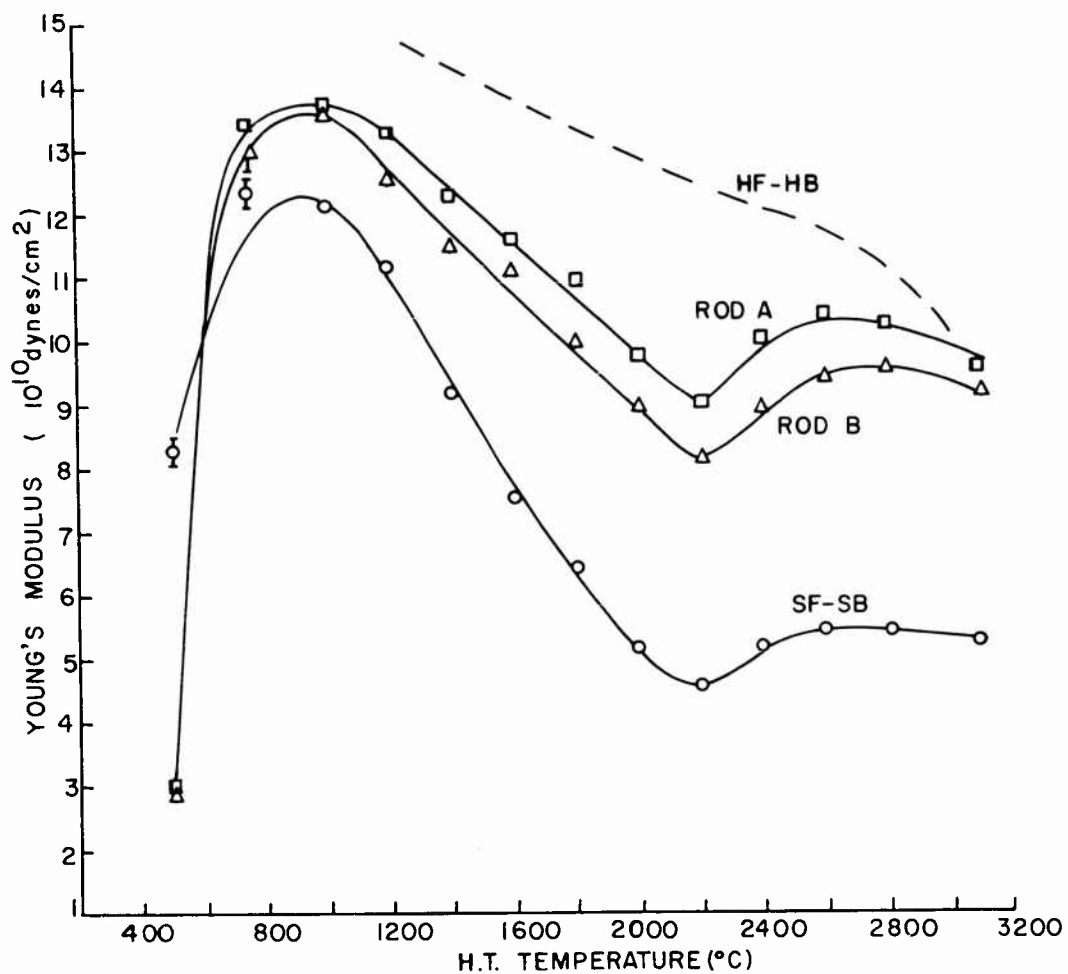


Fig. 1 Heat Treatment Dependence of the Young's Modulus for the Raw Coke Specimens

### III. ELASTIC PROPERTIES AT HIGH TEMPERATURE

#### A. Introduction

Recent developments in high temperature technology require advanced knowledge of the high temperature mechanical properties of graphite. Quite a lot of information has recently become available concerning the high temperature behavior of the mechanical properties of certain types of commercial graphites. However, there was very little information on the dependence of the elastic modulus on temperature for graphite materials made from various types of carbon and heat treated to various temperatures. Some preliminary results of measurements of static Young's modulus of carbons in bending at high temperature were reported already<sup>4, 6</sup>. The results presented there have been verified and extended using an improved measuring apparatus recently constructed.

The samples were laboratory prepared (coke binder and extruded) types of carbon (soft filler-soft binder, soft filler-hard binder, hard filler-soft binder and hard filler-hard binder) and a few special commercial graphites, namely pyrolytic graphite (General Electric Co.), ZTA graphite (National Carbon Co.) and glassy carbon (Tokai Electrode Co.). The ZTA and pyrolytic graphites are important from a purely scientific point of view since they are highly anisotropic; and also have important technical applications. A study of these basic carbon types might be helpful in comprehending the high temperature behavior of carbon materials.

#### B. Measuring Equipment

The principle of the measuring technique has been described previously<sup>3, 4</sup> and only a brief description of its operation is included here. The specimen to be investigated (1/2" dia. and 8" long) is held by graphite supports at two points 7" apart. The carbon sample mounted on these supports is placed in a 1-1/2" ID graphite tube which can be heated electrically to any desired temperature up to about 2500°C. The bending force is applied at the midpoint between the supports and the deflection of the specimen is measured by LVDT's placed 3" apart. The maximum deflection was limited to about 0.05 mm. Contact between the specimen and the LVDT core is accomplished through graphitized lampblack rods. The force is also applied to the specimen through a similar lampblack push rod and its magnitude is determined from the deflection of a calibrated cantilever. The two outer LVDT's are used to correct for any displacement which may be caused for instance by crushing at the sample supports.

Electronic circuits average out the two differences in deflection and an X-Y recorder gives the force-deflection curve whose slope is a measure of Young's modulus. The time required for recording the stress strain loop at a given temperature is about 20 seconds. Under these conditions creep effects were found to be negligible for ambient temperature within the measurement range, e.g. below 2400°C.

The electronics of the high temperature elasticity measurement apparatus used previously<sup>3, 4</sup> was improved by eliminating the troublesome servomotor system which had a narrow range of reproducible operation and had to be reset several times during a single series of experiments which in time led to extensive scattering in the resulting

data. In the new design\* the displacements which are measured by LVDT's are properly averaged before being amplified, rectified, and recorded. The detailed diagrams of the electronics associated with the measuring circuits were already presented in Part IV, Figs. 8, 9 and 10<sup>4</sup> and will not be reproduced here. This apparatus has an increased range of linearity due to the elimination of the troublesome servomotor and associated linkages. The graphite tube furnace is the same as previously used<sup>2,3</sup>.

### C. Test Samples

#### 1. Laboratory prepared samples--four basic types

The test specimens were 1/2" dia. extruded rods consisting of soft filler-soft binder, soft filler-hard binder, hard filler-soft binder and hard filler-hard binder. Raw Texas coke was used for the soft filler coke and the hard filler coke was prepared from phenol formaldehyde resin (Durez No. 175). These cokes were calcined in separate batches at 1200°C for several hours in the baking furnace before crushing, grinding, and sorting into the various particle sizes. Medium No. 30 coal tar pitch from the Barrett Co. was used as the soft binder and a laboratory prepared phenol benzaldehyde resin (PB) was used as the hard binder. When extrusion oil was needed, Vacwax 80 of Socony Vacuum Co. was used. The preparation procedure for the filler-binder mixture (green mix) was described previously<sup>1,2,7</sup>.

#### 2. Pyrolytic Graphite

Pyrolytic graphite specimens were obtained from Dr. R. J. Dicfendorf of the General Electric Co.<sup>8</sup> The technique used for preparing the pyrolytic graphite is in principle very simple, consisting of decomposing a carbonaceous gas on a hot surface<sup>9</sup>. However, the elementary processes involved are fundamentally very complicated and a complete characterization of the material requires knowledge of the temperature, pressure, flow rate, geometry, diffusion coefficients, rate constants for all reactions, as well as thermal conductivities and accommodation coefficients for the gaseous species. Pyrolytic graphite is interesting because of its high degree of orientation and very low porosity as well as absence of any binder material. The deposition temperature of the General Electric pyrolytic graphite was 2200°C and the sample was annealed for 30 min. in our graphitizer at 2200°C.

#### 3. ZTA Graphite

This graphite was obtained from the National Carbon Co. The process for the manufacture of high density graphite consists of compressing a graphite material at temperatures around 2500°C where graphite is quite plastic. The process is far from simple because of the extremes of temperature and pressure needed to attain the necessary plasticity and compaction. Hot working of graphite accomplishes more than densification--it results in a highly oriented graphite with properties intermediate between standard commercial graphite and the pyrolytic and single crystal graphite.

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\*The electronics was designed and constructed by D. C. Wobschall now at Roswell Park Memorial Institute, Buffalo, New York.

#### 4. Glassy Carbon

This so-called glassy carbon was prepared by Tokai Electrode Co. Glassy carbon is a highly cross linked carbonized resin containing no binder. The material is a highly gas-impermeable carbon with an appearance like glass. It is a very hard brittle material which can be cut only by a diamond cutter or an ultrasonic technique. X-ray diffraction studies of this material have shown that even after heat treatment to 3000°C, this carbon is still quite amorphous. This glassy carbon is interesting because it is a perfect example of an extreme case of hard carbon in which no crystalline phase is present.

#### 5. Low Density Carbon

This material was received from the Great Lakes Carbon Corp. According to a report by Stecker this sample is made from ingredients producing a typical soft carbon. The average apparent density is 0.64 g/cm<sup>3</sup>. There is on the market another low density carbon with a quite similar appearance (average density 0.65 g/cm<sup>3</sup>), known by the name "porous carbon" and developed by the Tokai Electrode Co. The manufacturing method is quite different than that of Great Lakes Carbon Corp. carbon and there is a patent pending at present. This material is made by thermal decomposition and carbonization of some kind of resin. This porous carbon is expected therefore to belong to the hard filler class as far as the behavior of the Young's modulus at high temperature is concerned. This would be another very interesting carbon to be examined but we could not get hold of an appropriate sample for our studies.

### D. Results and Discussion

#### 1. Temperature dependence of elastic modulus of Graphitized Bodies

##### a) Four basic laboratory prepared types of carbon

Specimens of the four types of laboratory prepared carbons were heat treated to 3000°C before mounting in the high temperature elasticity apparatus. Fig. 2A shows the Young's modulus data for these rods as a function of temperature up to 2300°C. The measured points are shown by open and filled-in points of the same shape for increasing and decreasing temperature respectively. Even though observable viscous creep sets in around 2000°C, reliable force-deflection measurements could be obtained because of the small applied force used and the correspondingly small magnitude of the deflection and the speed of operation of the equipment. The usual maximum in Young's modulus is observed only for the rods with soft filler whereas bodies with hard filler show a continuous decrease in modulus with increasing temperature. The fact that there is a maximum for the soft filler bodies and no maximum for the hard filler bodies shows that the behavior of Young's modulus vs. temperature depends primarily on the filler material. A similar conclusion was reached previously by Davidson et al<sup>10</sup> and also in our experiments on the dependence of the room temperature Young's modulus on the heat-treatment temperature presented previously<sup>2,7</sup>. The results indicate that a study of the dependence of the strength of hard filler bodies on temperature would be a worthwhile undertaking to check if such carbons show a maximum in strength around 2500°C as do the soft filler graphites.

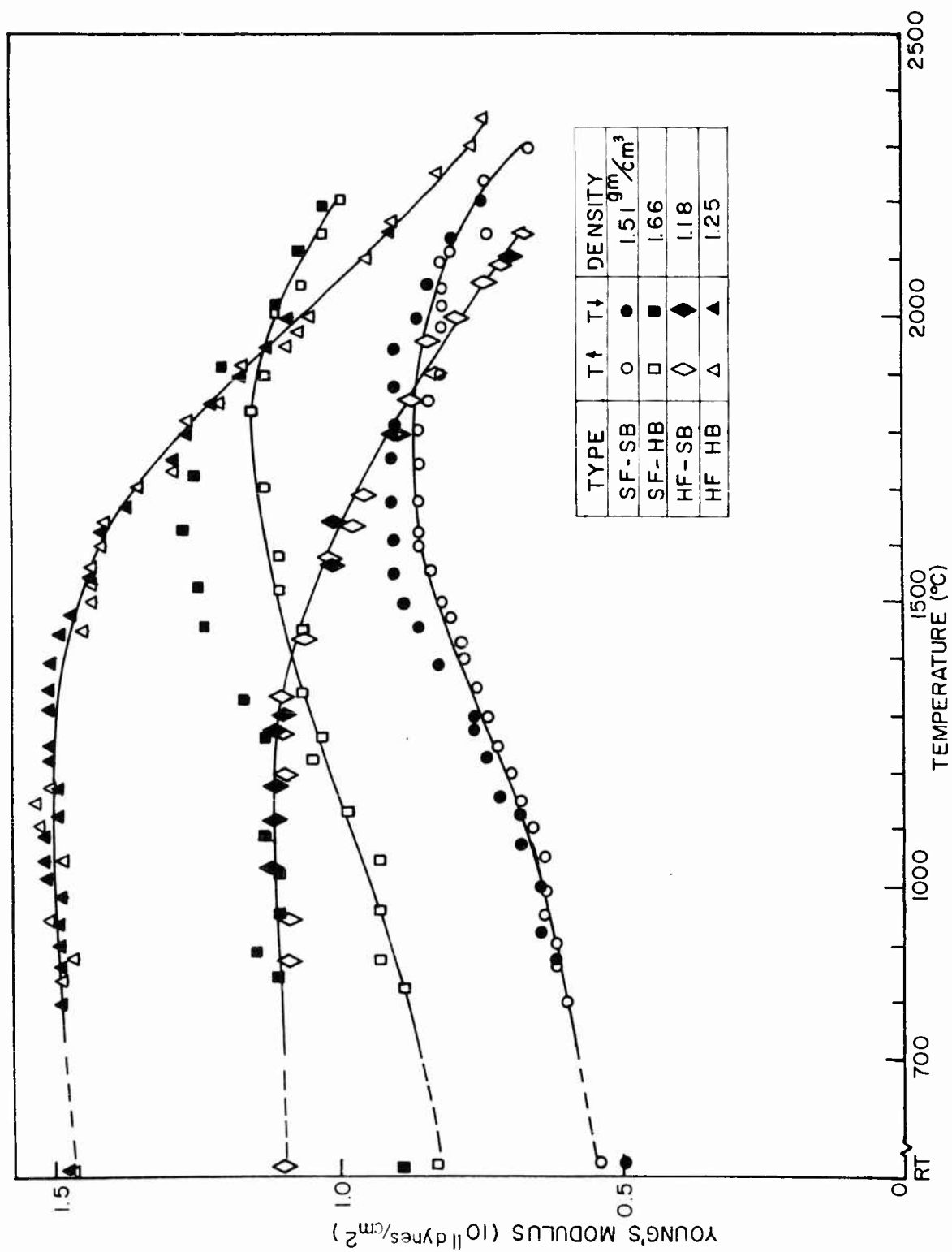


Fig. 2A Young's Modulus vs. Ambient Temperature for Four Types of Graphitized Carbon Bodies

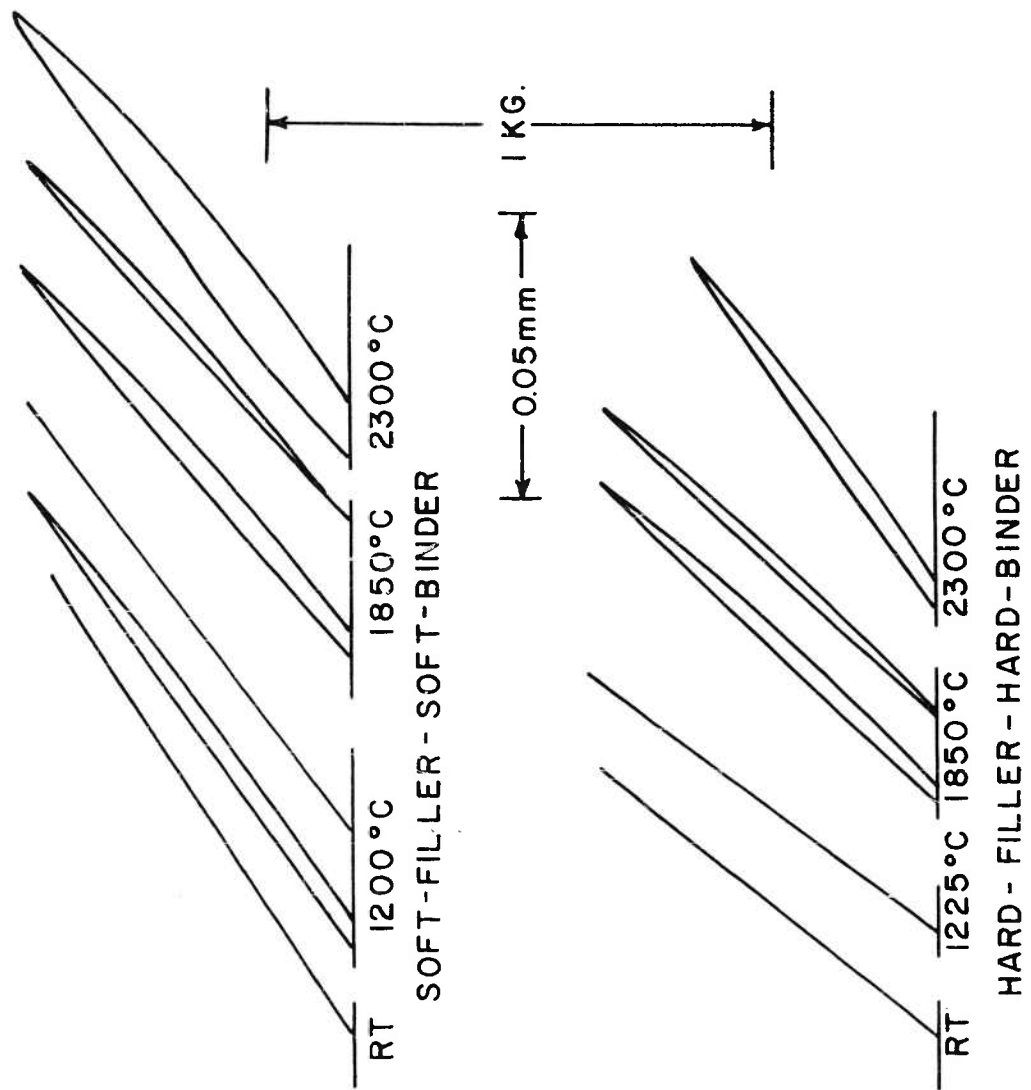


Fig. 2B Tracings of Recorded Force-Deflection Curves at Various Temperatures for SF-SB and HF-HB Rods

b) Pyrolytic Graphite

The elastic modulus results for pyrolytic graphite are shown in Fig. 3. The deposition temperature of this sample was 2200°C. The load direction was normal to grain layers. Fig. 3 shows that the elastic modulus increases up to about 1600°C, followed by a decrease beyond this temperature. Pyrolytic graphite therefore has at least in the grain direction a behavior analogous to a soft filler material.

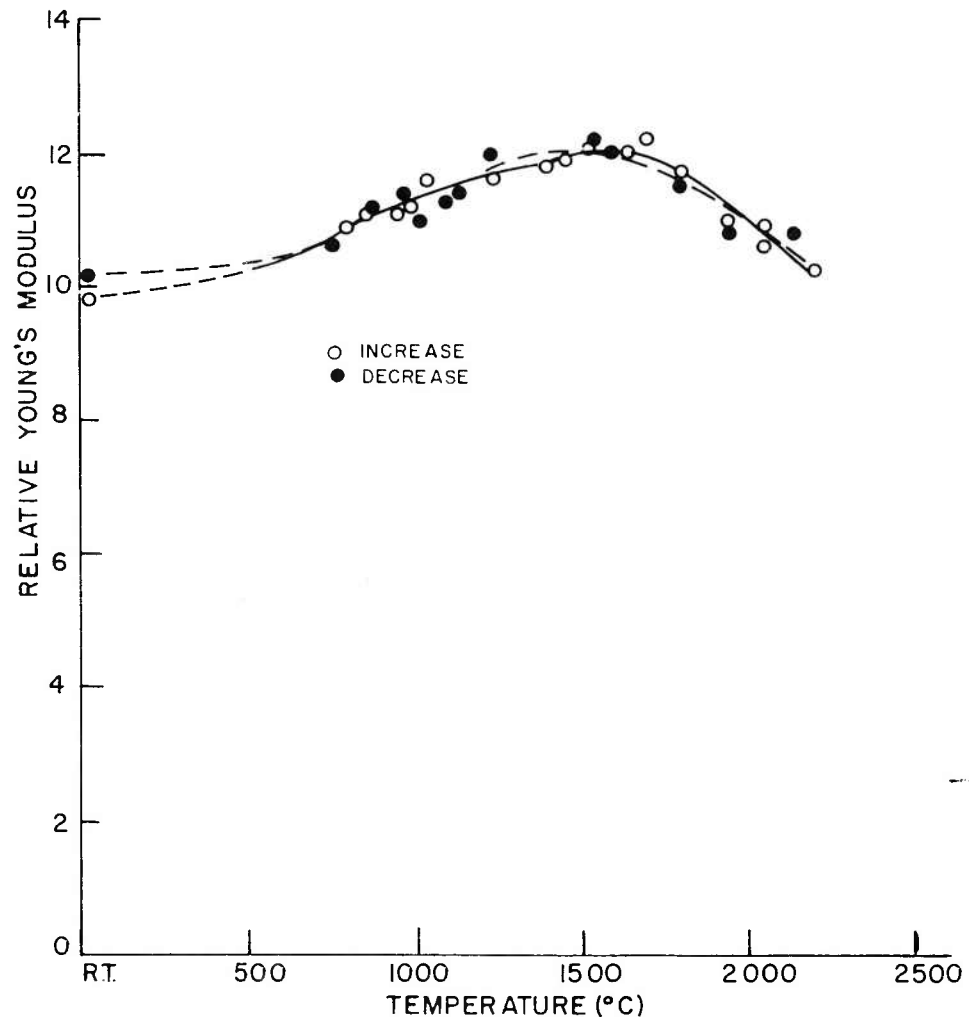


Fig. 3 Relative Young's Modulus as a Function of the Ambient Temperature for Pyrolytic Graphite (Load Direction is Normal to Grain Layer)

c) ZTA Graphite

The Young's modulus of ZTA graphite was measured in the room temperature elasticity apparatus to investigate the influence of the grain orientation on the Young's modulus. Fig. 4 shows Young's modulus data for a ZTA graphite rod as a function of temperature up to 2400°C among others for the case of the sample cut out with the axis perpendicular to the molding direction and the load applied in the molding direction.

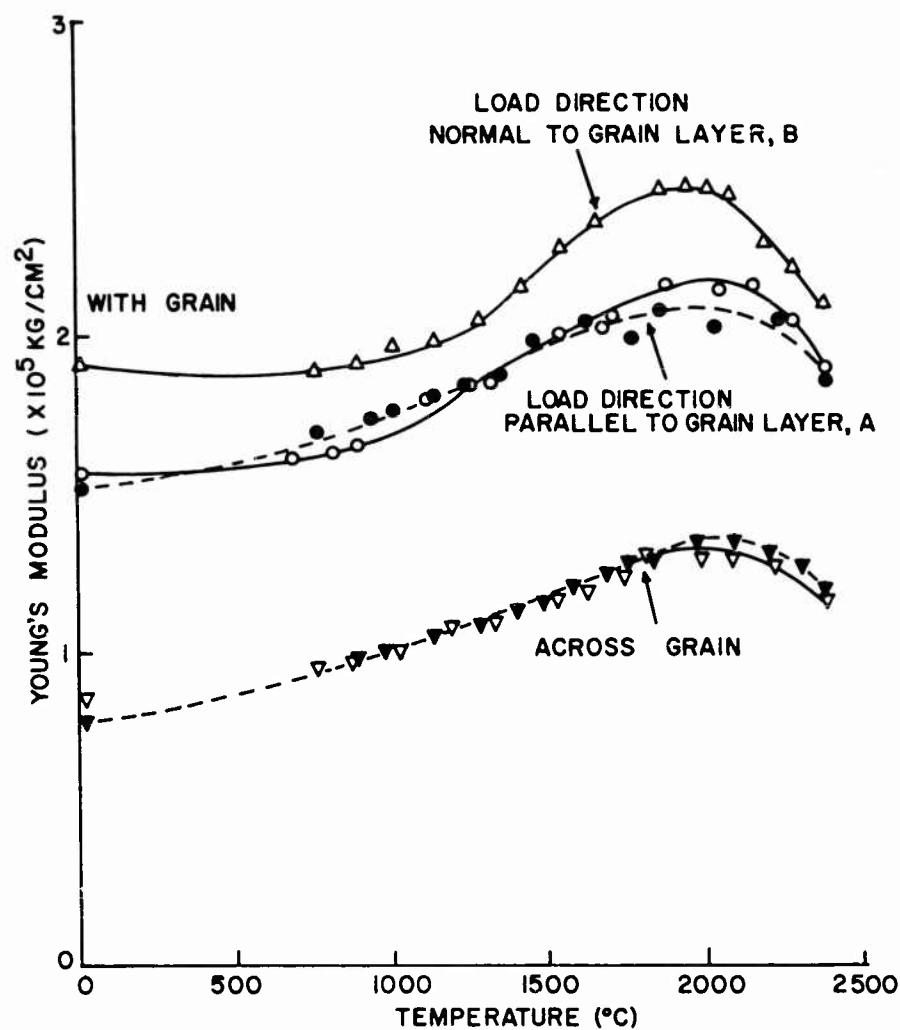


Fig. 4 Young's Modulus as a Function of the Ambient Temperature for ZTA Graphite Rod (Density  $d = 1.955$ )

Measurements of the above sample in rotated position such that the load direction is perpendicular to the molding direction give a similar curve with a factor of 2 increase in Young's modulus. The values obtained for a sample cut out with the axis parallel to the molding direction are similar to the second case above but about 5 percent lower. The results show that in all three cases the maximum Young's modulus occurs at 2000°C. The elastic behavior of ZTA graphite is therefore similar to soft filler rods but having the maximum of Young's modulus shifted slightly to a higher temperature.

## 2. Temperature Dependence of the Elastic Modulus of Carbon Rods while Heat Treatment is Progressing

In this work a specimen which was previously heat treated to about 1000°C was mounted in the furnace and force-deflection measurements made throughout the temperature range 750°C to a temperature exceeding the previous heat-treatment temperature after which the rod was cooled to room temperature. Measurements were continued using the same procedure, increasing stepwise the maximum temperature by 400°C in each run. The heating rate of the furnace was about 300°C per hour and holding time at the maximum temperature about 20 min. The maximum temperature up to which measurements were performed was 2400°C, this limitation being dictated by the onset of rapid viscous creep. Typical data is shown in Fig. 5 for a soft filler-soft binder rod having a heat-treatment temperature of 1600°C. For increasing temperature Young's modulus follows the upper curve (curve A) over a maximum up to the original heat-treatment temperature of 1600°C and then further down, up to 2000°C; for decreasing temperature it follows the curve B on which it again goes over a maximum. Reheating the same specimen gives curve C which above 2000°C appears as an extension of curve A. Cooling from this temperature down gives curve D which shows a marked stiffening in the range 1600° - 2400°C.

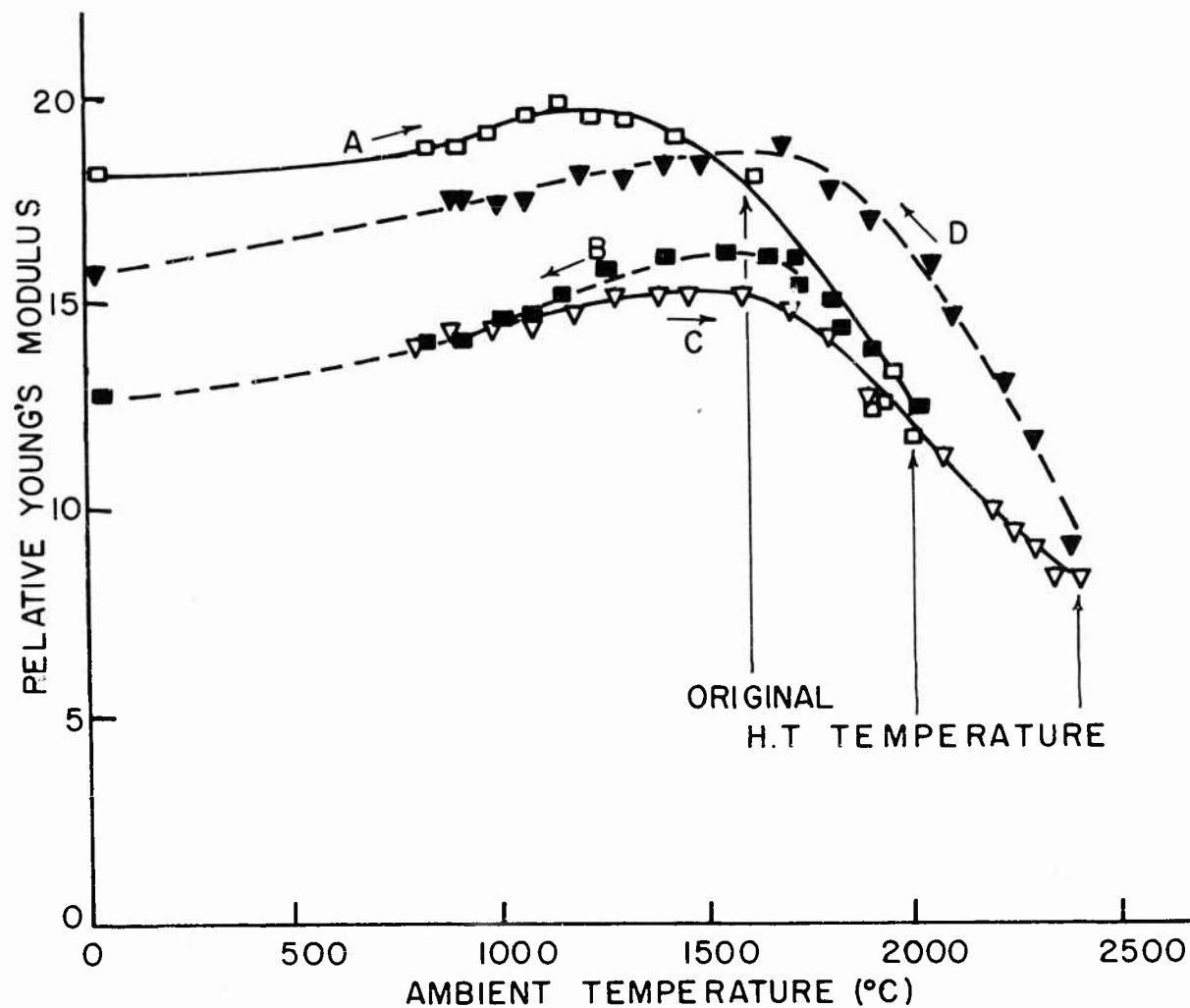


Fig. 5 Typical Curves for the Dependence of Young's Modulus on Temperature for a SF-SB Rod having an Original Heat-Treatment Temperature of  $1600^{\circ}\text{C}$ . The Measured Points are Shown by Open and Filled-in Points of the Same Shape for Increasing and Decreasing Temperature, Respectively. Sample Heat Treated Prior to Measurement  $1600^{\circ}\text{C} - 2000^{\circ}\text{C}$

a) Soft filler-soft binder

A complete family of curves for soft filler-soft binder rod is shown in Fig. 6. The heat-treatment temperature of the specimen when first inserted into the furnace was  $1000^{\circ}\text{C}$ . The solid curves are for increasing temperature and the broken

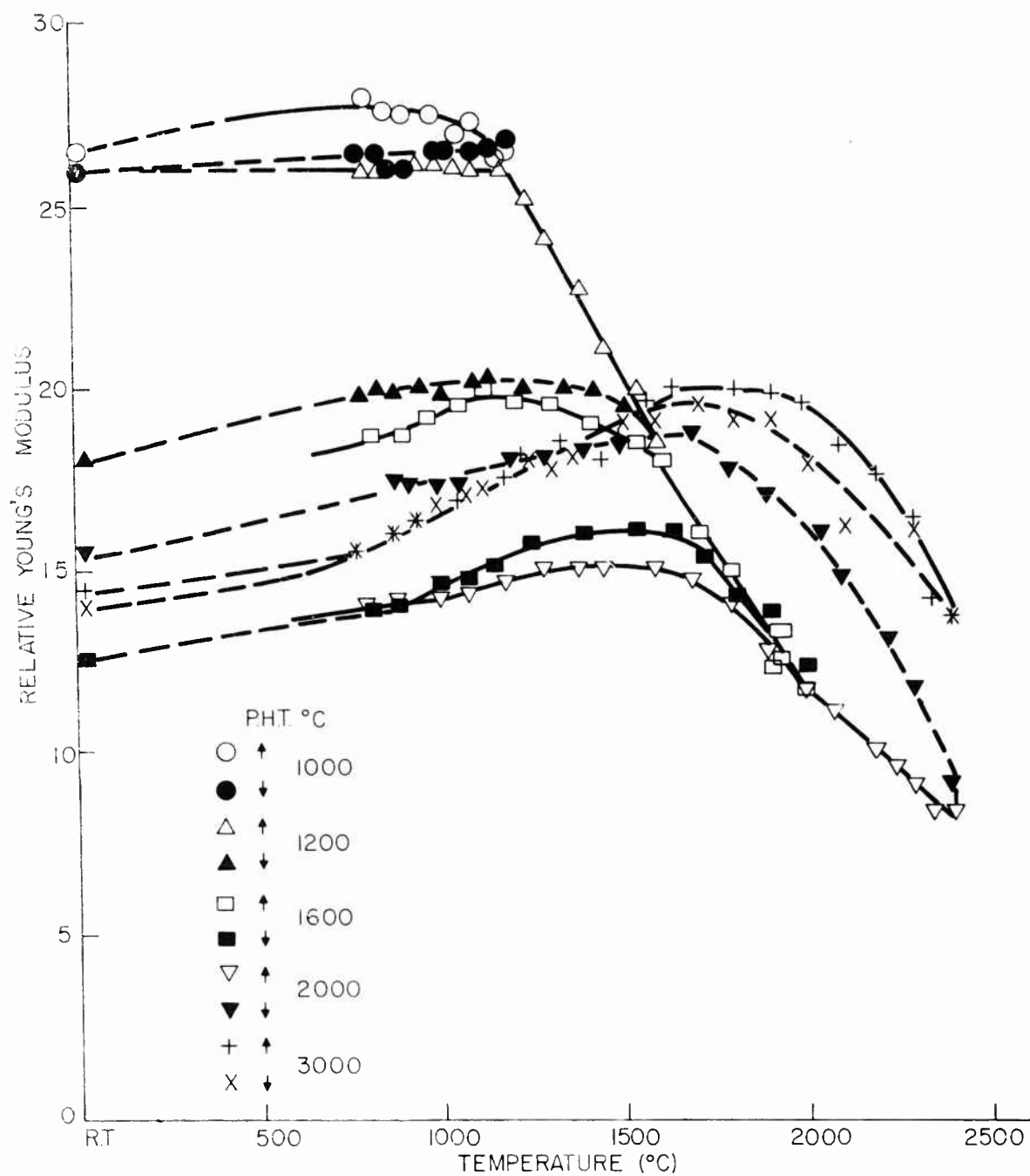


Fig. 6 Young's Modulus as a Function of the Ambient Temperature for a SF-SB Rod

curves are for decreasing temperature. The measured points are shown by open and filled-in points of the same shape for increasing and decreasing temperature, respectively. The general behavior obtained here with the new electronics does not differ radically from that obtained previously<sup>4</sup>. The essential features of the results observed are: 1) a general decrease in Young's modulus with increasing temperature while the rod is being heat treated, that is for temperatures above the highest previous heat-treatment temperature, 2) the presence of a maximum in Young's modulus somewhat below the maximum heat-treatment temperature for all variously heat treated samples, 3) an increase of the modulus above the heat treatment curve at temperatures above 1600°C. The heat treatment dependence of room temperature Young's modulus taken from the above measurements is similar to the general behavior previously reported in the work with the room temperature elasticity apparatus<sup>2</sup>.

b) Soft filler-hard binder

Similar systems of curves have been obtained for soft filler-hard binder carbon specimens. The heat-treatment temperature of the specimen when first inserted into the furnace was about 900°C. Fig. 7 shows the Young's modulus as a function of the ambient temperature for both increasing and decreasing temperatures. The increasing temperature curve for pre-heat treatment temperature 1600°C was not measured below 1900°C because of equipment failure. The dependence of the room temperature Young's modulus values on the maximum heat-treatment temperature obtained from this specimen are quite similar to those obtained from the soft filler-soft binder specimen discussed in previous section.

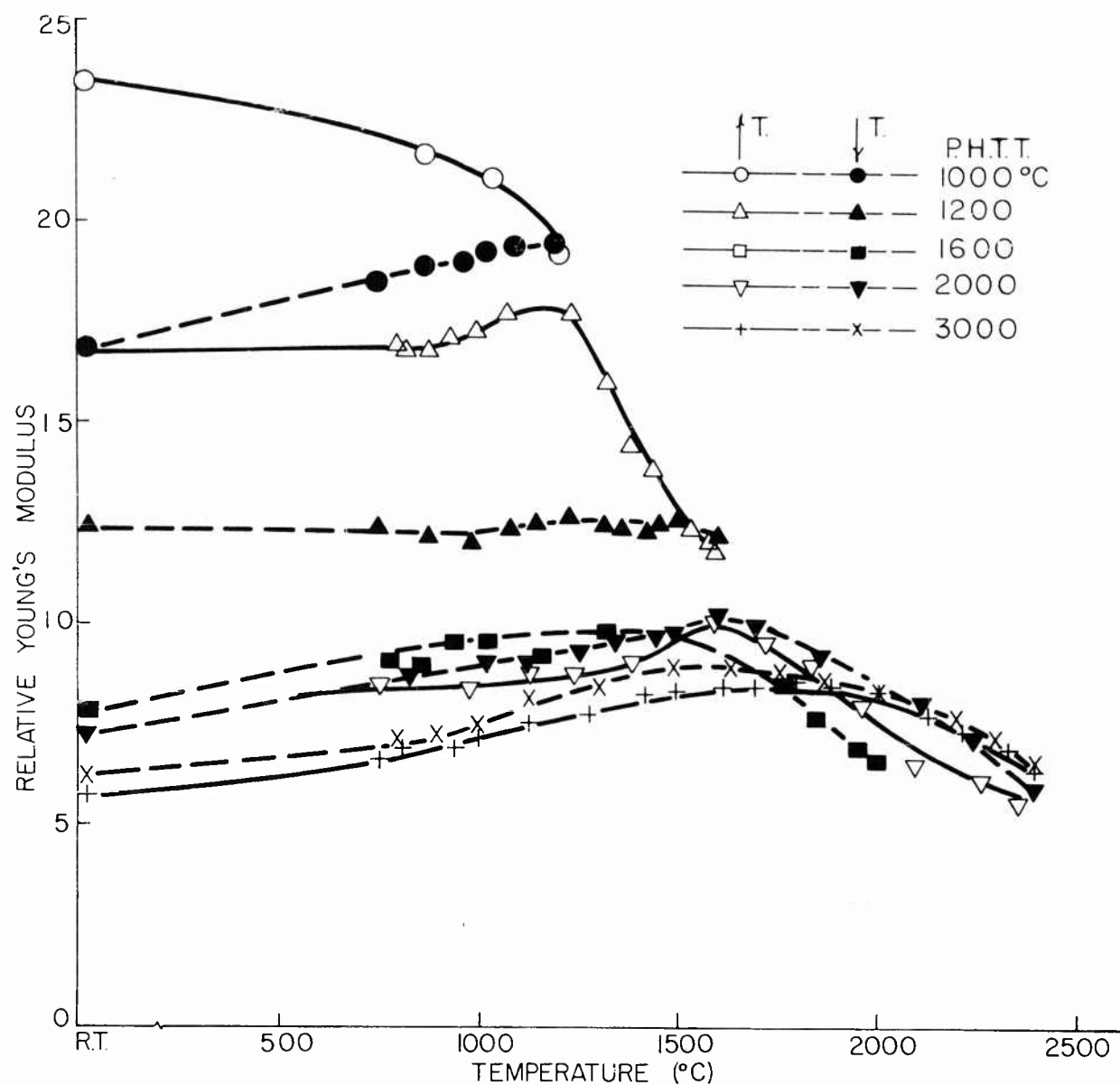


Fig. 7 Relative Young's Modulus as a Function of the Ambient Temperature for a SF-HB Rod

c) Hard filler-soft binder

Elasticity measurements have been made on a hard filler-soft binder rod whose original baking temperature was 700°C. The temperature dependence of Young's modulus is shown in Fig. 8. Some of the curves show a very slight maximum and

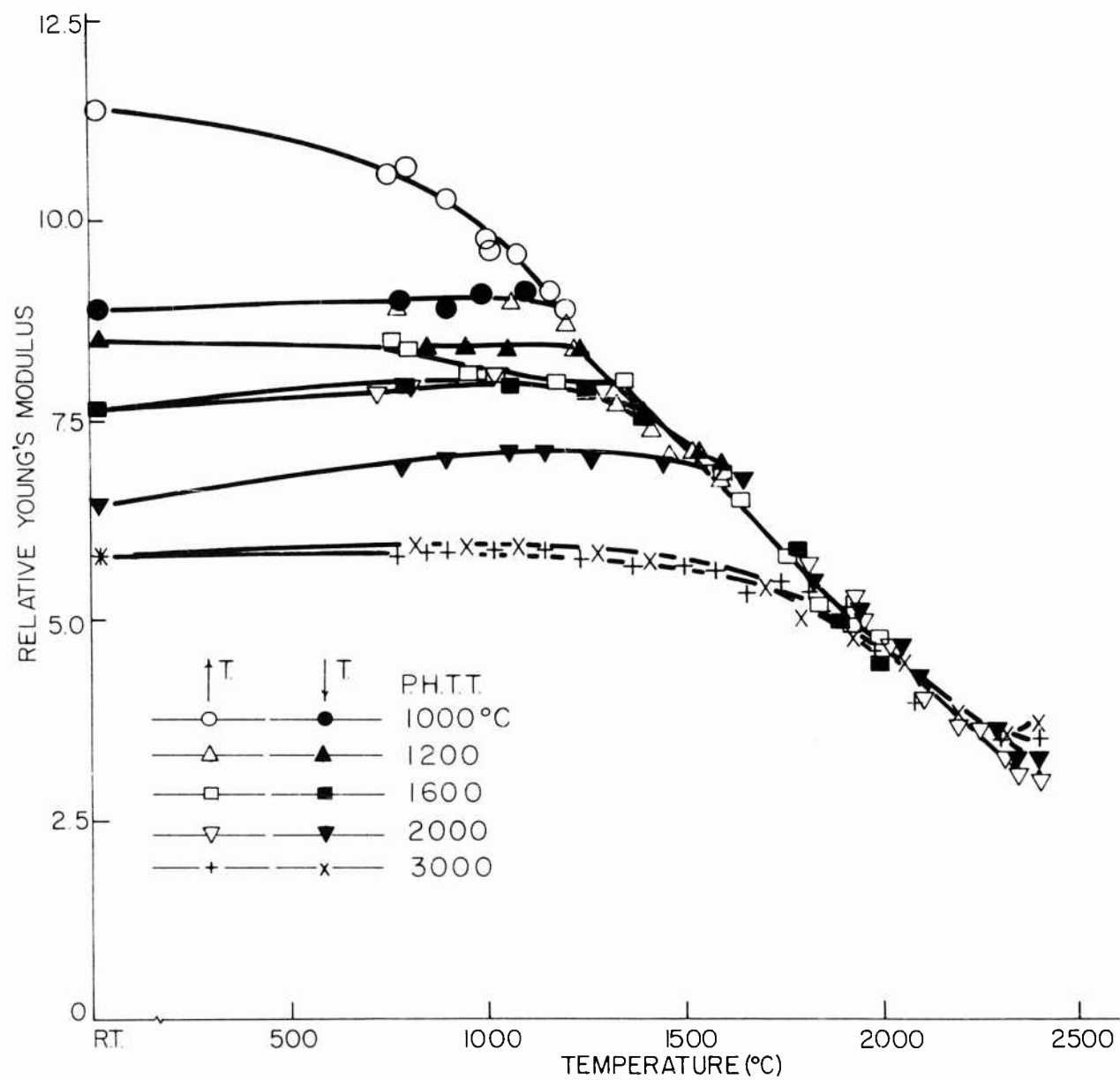


Fig. 8 Relative Young's Modulus as a Function of the Ambient Temperature for a HF-SB Rod

others show no maximum at all. During heat treatment the modulus of this material decreases nearly continuously up to 2400°C and possibly also beyond. The heat treatment dependence of the room temperature Young's modulus taken from the above measurements is similar to the general behavior previously reported<sup>2</sup>.

d) Hard filler-hard binder

A similar system of curves has been obtained for a hard filler-hard binder carbon specimen whose original heat-treatment temperature was 1000°C. Fig. 9 shows the Young's modulus as a function of the ambient temperature for both increasing and decreasing temperature. All the curves show a continuously decreasing modulus with increasing ambient temperature. The dependence of the room temperature Young's modulus of these rods on heat-treatment temperature is also similar to the previously observed behavior<sup>2</sup>.

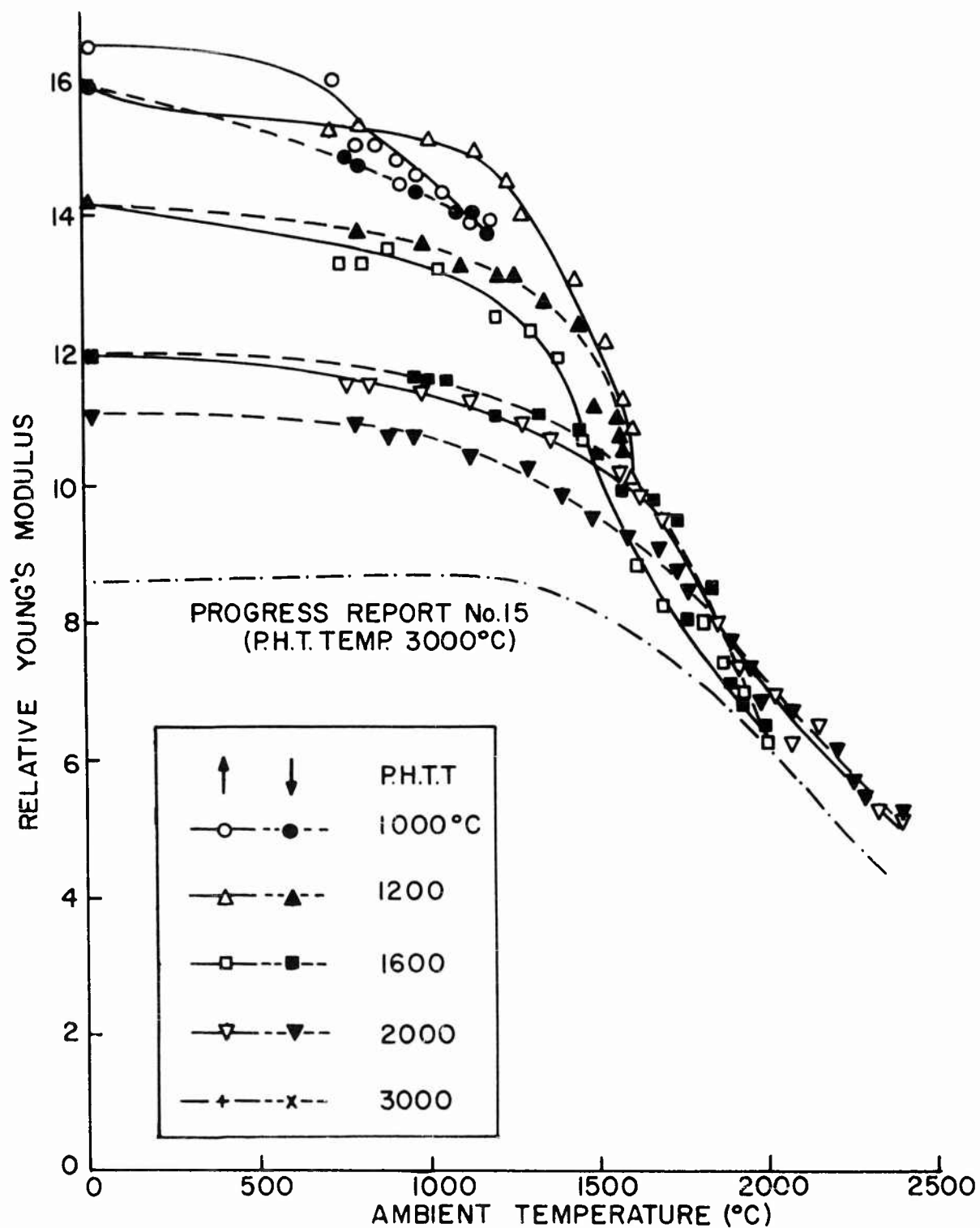


Fig. 9 Relative Young's Modulus as a Function of the Ambient Temperature for a HF-HB Rod (Z-1)

e) Glassy carbon

Elasticity measurements have also been made on a glassy carbon plate whose original baking temperature was 1000°C. The sample dimensions were 1.56 cm wide x 0.3 cm thick x 20 cm long. The results of the elasticity measurements are shown in Fig. 10. The curves in Fig. 10 show that during heat treatment the modulus decreases

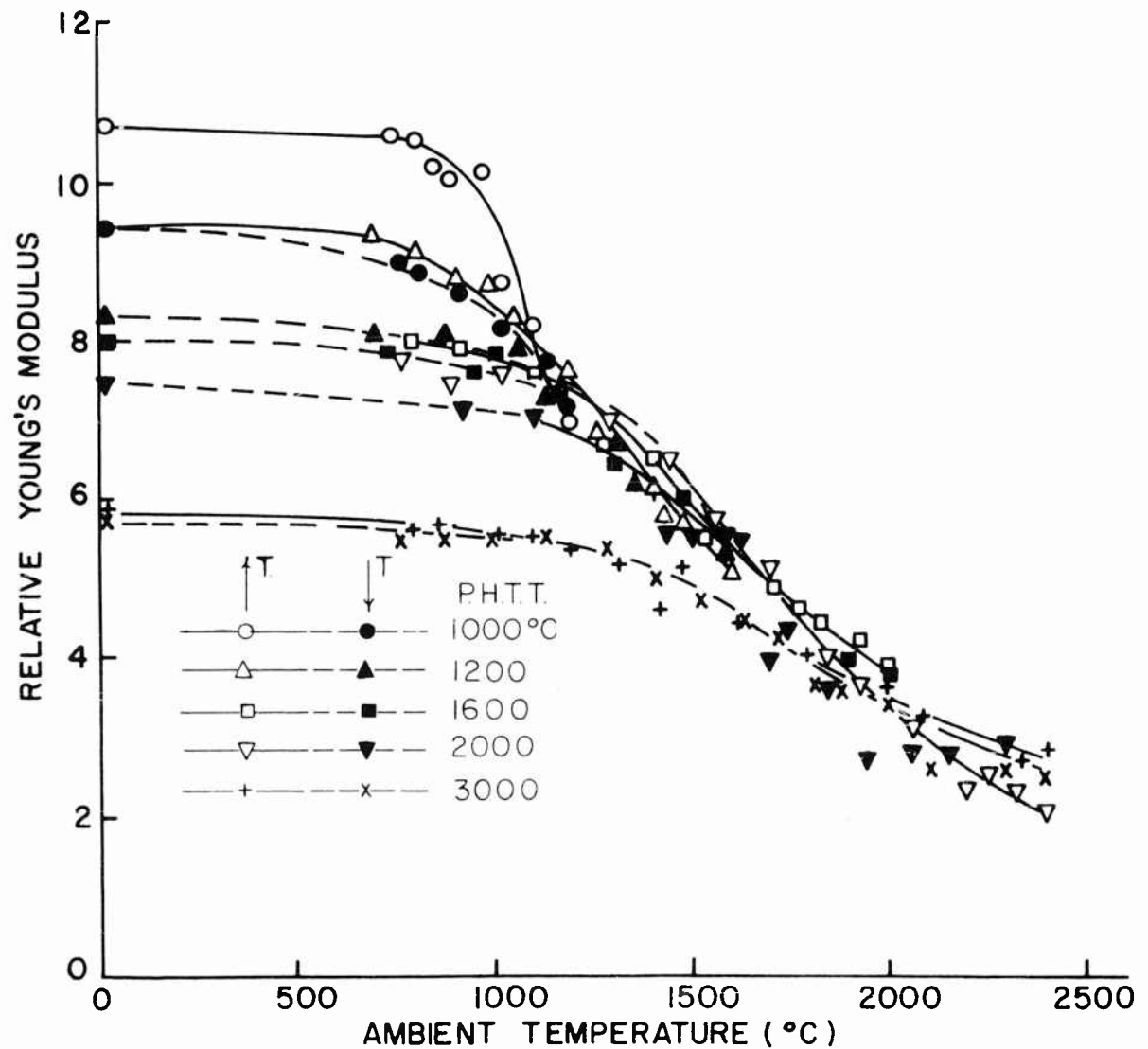


Fig. 10 Relative Young's Modulus as a Function of the Ambient Temperature for a "Glassy Carbon" Plate

continuously up to 2400°C. The heat treatment dependence of the room temperature Young's modulus taken from the above measurements are shown in Fig. 11. It is interesting to note that the slope of the curve is similar to the one for hard filler carbon bodies. Glassy carbon is a thermally decomposed resin which is carbonized in an inert atmosphere. The dotted curve in Fig. 11 shows the average Young's modulus as obtained by one of the authors (S.S.) from 10 rods (5 cm dia. 130 mm long) by means of an ultrasonic pulse technique, the work having been performed at the Japan Atomic Energy Research Institute.

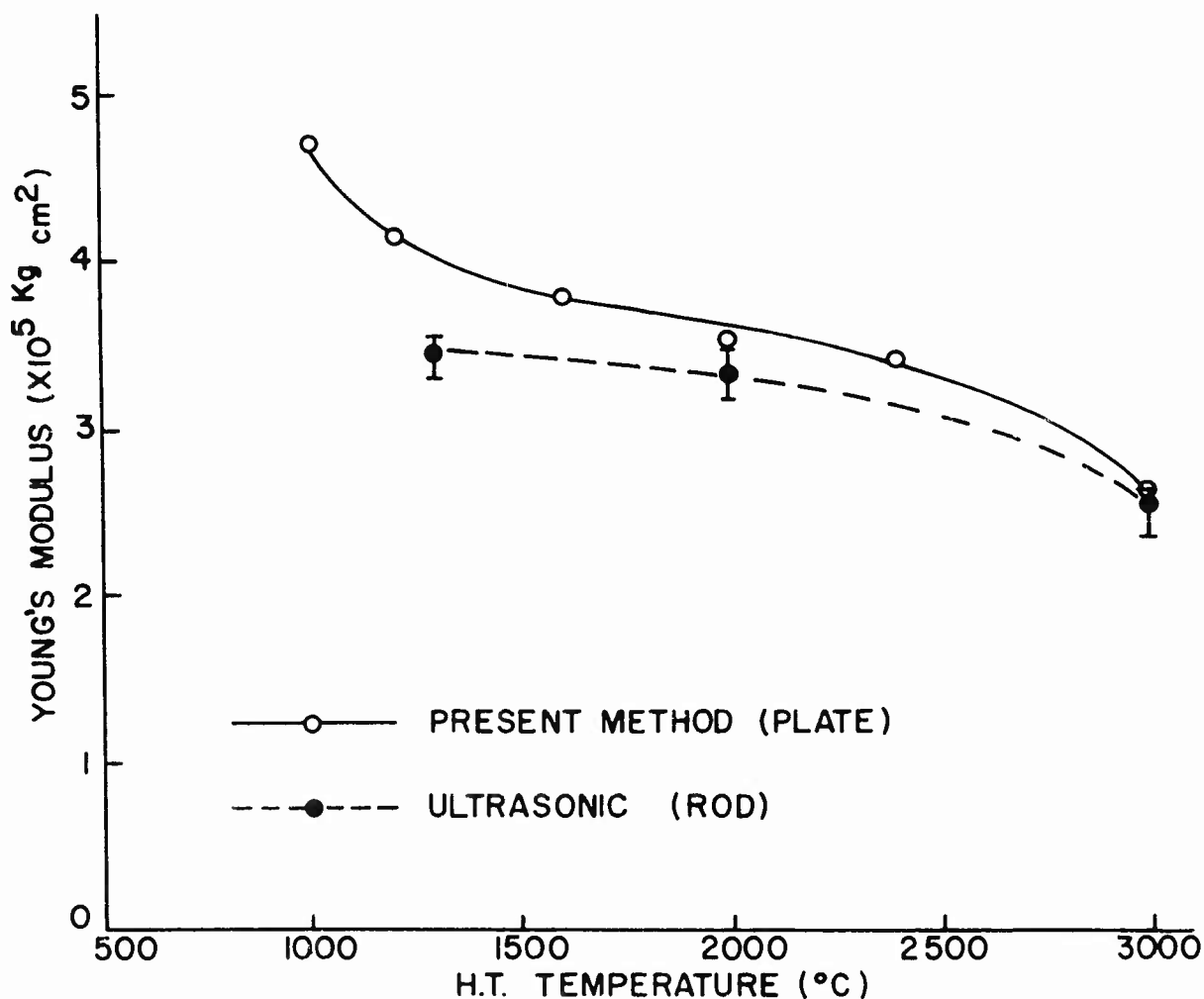


Fig. 11 Room Temperature Young's Modulus as a Function of Heat-Treatment Temperature for a "Glassy Carbon" Plate

f) Low density carbon

The original heat-treatment temperature of the specimen obtained from G.L.C.C. is not known but it is probably around  $1000^{\circ}\text{C}$ . To make sure, the sample was heat treated at  $1500^{\circ}\text{C}$  for 15 min. Thereafter the temperature dependence of Young's modulus of this sample was measured while the heat treatment was progressing up to  $1800^{\circ}\text{C}$ . Then the measurements were repeated until  $2100^{\circ}\text{C}$  and  $2400^{\circ}\text{C}$  were reached. Fig. 12 shows the change of Young's modulus in the heating-up process.

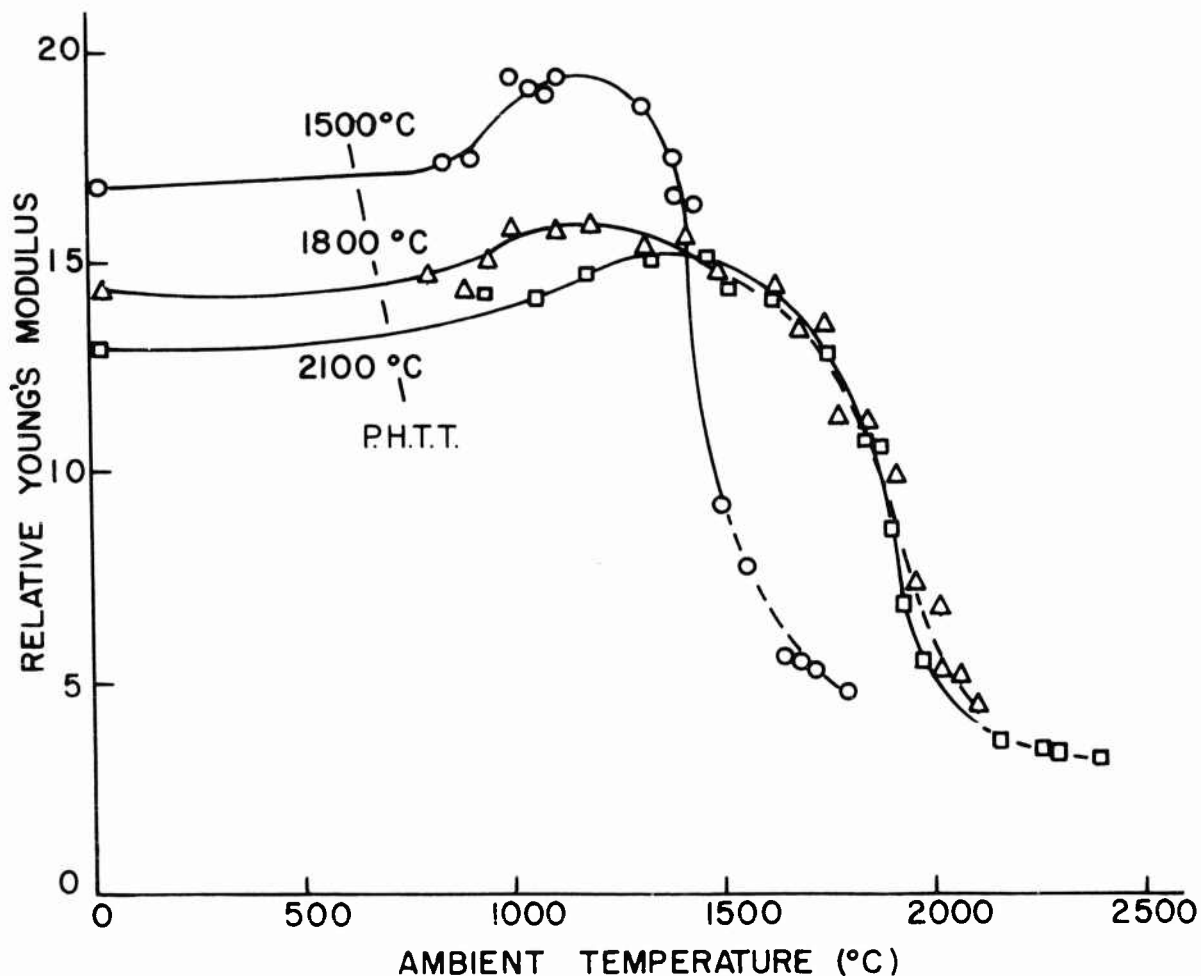


Fig. 12 Relative Young's Modulus as a Function of the Ambient Temperature for a Low Density Carbon Rod (B-1) (Density:  $0.640 \text{ g/cm}^3$ )

The presence of maxima in the modulus at a temperature somewhat below the corresponding heat-treatment temperature for all previously heat treated samples is clearly visible. The modulus decreases with increasing temperature for temperatures above the highest previous heat-treatment temperature. The material has such a terrible volume shrinkage that measurements above the highest previous heat-treatment temperature have little accuracy; holding the samples in position is difficult since they become loose. Therefore the part exceeding the previous heat-treatment temperature is shown by a dotted line and for the same reason curves for decreasing temperature are not given at all. The shrinkage values were observed for the initial heat treatment cycle to 1500°C; the volume shrinkage amounts to about 5 percent and at 2100°C it is about 10 percent.

Fig. 13 shows the change of room temperature Young's modulus with heat-treatment temperature and the decrease in volume with heat treatment in which the original heat-treatment temperature was assumed to be roughly 1000°C.

#### E. Conclusions

The elasticity measurements presented in this paper show that the nature of the filler material is much more influential than the nature of the binder in determining the behavior of the temperature dependence of Young's modulus of a carbon. The modulus of soft filler rods shows the following behavior: 1) a general decrease in the elastic modulus with increasing temperature above the highest previous heat-treatment temperature and 2) the presence of a maximum in the elastic modulus at a temperature somewhat below the maximum heat-treatment temperature. The carbon made with hard filler shows also a decrease above highest heat-treatment temperature, but no maximum below heat-treatment temperature for hard binder and only slight maxima for soft binder. These differences demonstrate the importance of the filler material in determining the elastic modulus behavior and might be used in describing the character of materials whose manufacturing processes are quite different. The results of measurements on pyrolytic and ZTA graphites have shown the temperature dependence of Young's modulus are similar to soft filler bodies. On the other hand, the results for glassy carbon show that the temperature dependence of its Young's modulus is as for a typical hard carbon body.

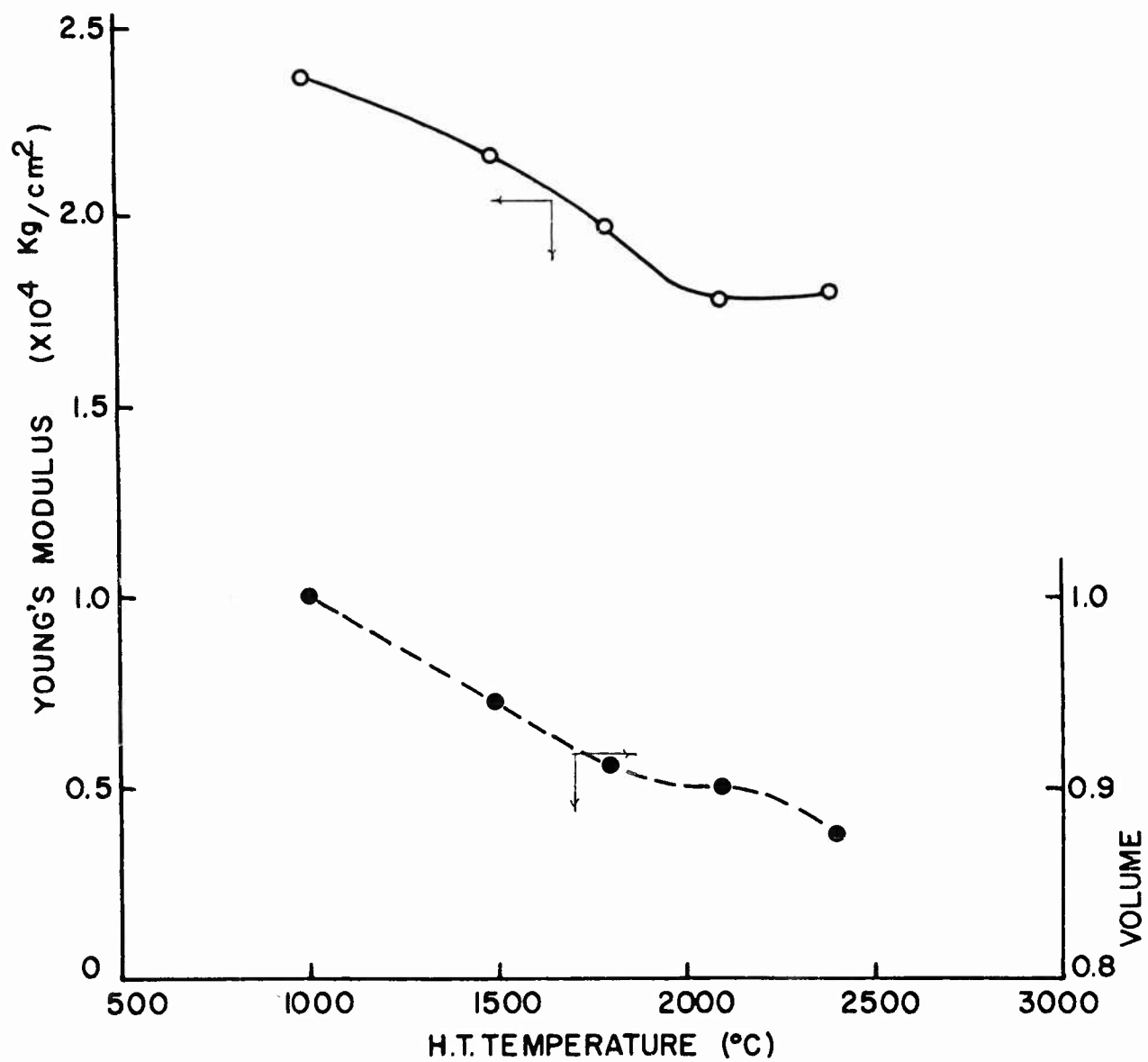


Fig. 13 Room Temperature Young's Modulus and Volume as a Function of Heat-Treatment Temperature for a Low Density Carbon (B-1)

#### IV. MECHANICAL ENERGY LOSSES

##### A. Introduction

One of the authors has recently in collaboration with Kobayashi<sup>11</sup> reported some results of preliminary investigations of internal energy dissipation in carbon materials. Under the present contract efforts were made to get more detailed information by repeating a number of experiments under a variety of conditions. In this report the newly obtained results are presented and a discussion of the loss mechanism in terms of motion of dislocations and other defects is given.

A great amount of information on crystal defects in graphite has been provided by studies of a number of investigators in recent years<sup>12-18</sup>. One can hope therefore that in the not very distant future the mechanical properties of graphite, as well as of other carbon solids, will become well understood from the microscopic point of view. However, the big difficulty is that one has not yet had good single crystals of graphite large enough for mechanical tests. At present, one has to study polycrystalline specimens which are not only porous but also full of structural irregularities. Even for such specimens the mechanical properties are probably mostly dependent on the behavior of crystal defects which however exist in such complicated environment as to be theoretically not tractable. For instance, to the authors knowledge various high temperature creep tests on graphite gave such different values for the activation energy that no definite identification of the corresponding elementary process could be obtained.

The analysis of the internal friction in terms of crystal defects is somewhat easier for the following reasons: 1) the experiments can be performed at such small strain amplitudes (ranging from  $10^{-3}$  or  $10^{-4}$  down to  $10^{-6}$  or even  $10^{-7}$ ) that the motion of each defect is controlled in accordance with the mobility; 2) the contributions of various mechanisms can be separated by observing the characteristic relaxation spectrum. For example, if the following Arrhenius type expression for the relaxation time is applicable:

$$\tau = \tau_0 \cdot \exp(H/kT) \quad (1)$$

the temperature dependence of internal friction  $Q^{-1}$  would give such a spectrum as mentioned above. It seems that in the case of carbon materials the study of the character of the mechanical energy loss provides a good tool for the investigation of the dynamical nature of dislocations as well as other crystal defects.

##### B. Experimental Method and Specimens

###### 1. Apparatus

The experimental arrangement used in this work (especially as far as the electric circuit is concerned) was very similar to the one used in the previous work i. e., in short a sample was vibrated by driving it electromagnetically and the vibrations detected using a pair of earphone coil transducers. The damping factor  $Q^{-1}$  of the first mode resonance curve was taken as a measure of internal friction but the frequency determination was made by means of an electronic counter instead of a direct reading from the dial scale of the oscillator as it was done before<sup>11</sup>.

The experiments on amplitude dependence of the energy loss at room temperature were made by using transversal vibrations of 6-4 in. long slabs the frequency of which was ranging between 250-2600 c/s. On the other hand, a resonance bar technique for longitudinal vibration frequencies between 10-20 kc was used in the low temperature experiments. A drawing of the sample holder and cryostat system is shown in Fig. 14. A cylindrical test piece about 4 inches long is supported at the middle by two needles facing each other in the common horizontal plane. In order to avoid external disturbances intervening in the samples' vibration the needles had to be only in light contact with the sample itself, while being rigidly fixed to the outer holder. When the coolant was liquid hydrogen the inner Dewar vessel was surrounded by another container filled with liquid nitrogen. To avoid possible troubles originating from moisture absorbed on the specimen, the sample chamber was evacuated and heated to 60°C before starting a run. Pure helium gas was flown through the chamber. By combination of controlled flow of gas and of electric power supplied to the heater, quite constant cooling and heating rates could be obtained (about 0.5°C/min.).

## 2. Specimens

First, specimens were made from two representative commercial carbons: polycrystalline graphite of reactor grade and baked carbon for crucible use. The reactor grade graphite was formed by extrusion and heat treated to 2800°C in an atmosphere containing fluorine for purification. Its density ranged between 1.67 - 1.69 and its impurity content was about  $2 \times 10^{-5}$ . The baked carbon was a molded block heat treated to 1200°C. Its density was quite high, ranging between 1.82 - 1.86.

Next, a glassy amorphous carbon prepared from a highly cross linked resin without using any binder (product of Tokai Electrode Mfg., Co.) and heat treated to 1000°C was examined as a perfect example of extremely hard carbon. It has been found by means of an X-ray diffraction that even after heat treatment to 2000°C no crystalline phase is present in this material.

Finally, two pyrolytic graphite specimens prepared at General Electric Research Laboratory were investigated. One of these samples was an as-deposited at 2200°C from methane gas at a pressure as low as 20 mm Hg. As well known, in such specimen the microcrystallites are aligned nearly parallel to the surface of deposition. However, even such graphite exhibits still a somewhat coarse appearance due to the so-called cone structure which indicates that the parallel alignment of the crystallites is not quite perfect. The second specimen was originally obtained by the same method mentioned above but was further heat treated to 3700°C at the General Electric Laboratories. During this latter heat treatment an appropriate tensile stress was applied so as to improve the crystalline alignment. Thus, an excellent graphite specimen exhibiting quite glossy appearance was obtained. The electric resistivity of this specimen was about  $5 \times 10^{-5}$  ohm-cm, of the same order as that of single crystals of graphite in the a-direction. Hereafter this specimen will be called "two dimensional graphite." The density of these pyrolytic graphites both as-deposited and the two dimensional was found to be above 2.2, thus indicating the presence of very few internal pores.

## 3. Neutron Irradiation

Samples of polycrystalline graphite of glassy carbon and of the two-dimensional graphite were irradiated in a 1 MW swimming pool type reactor on the

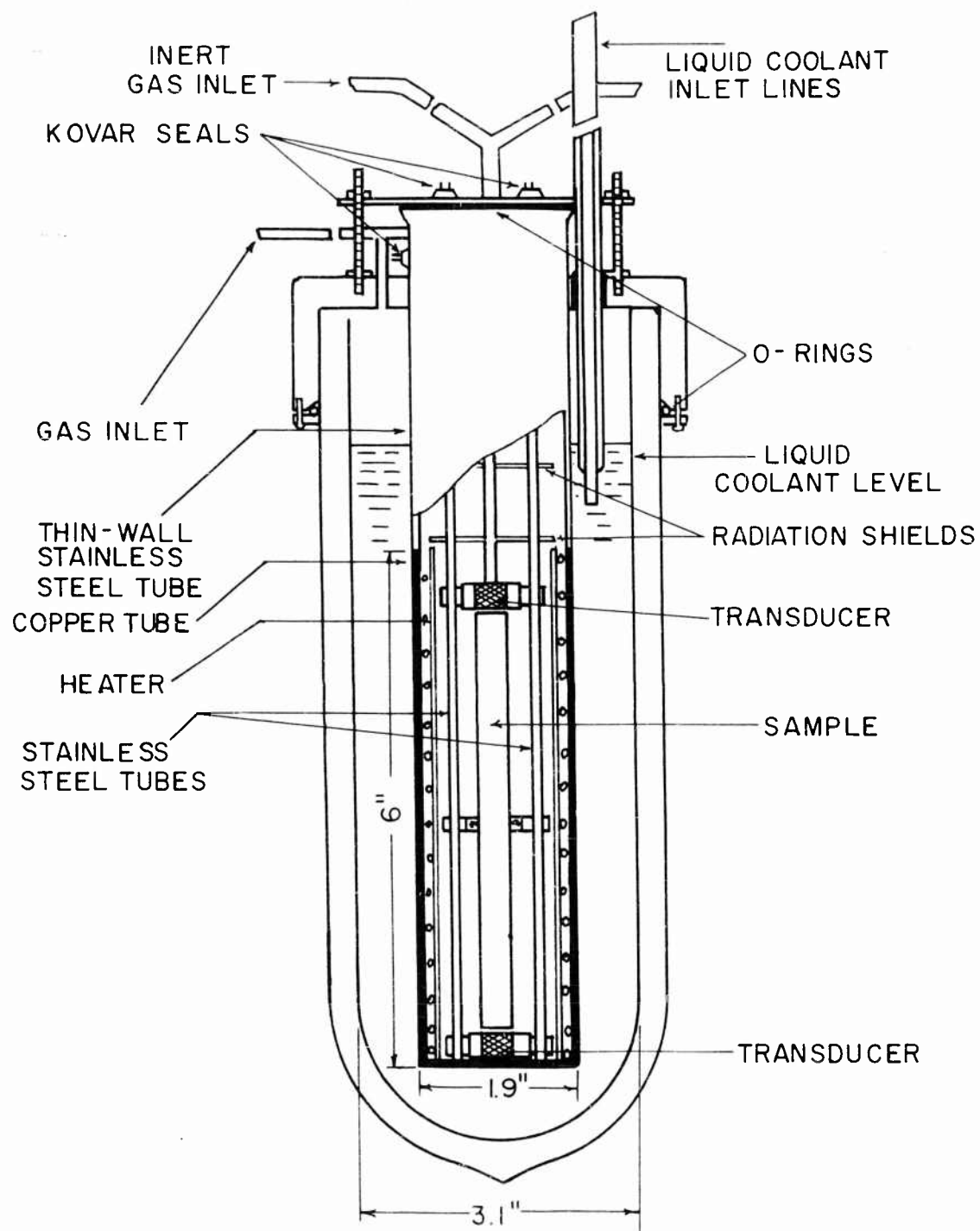


Fig. 14. Diagram of the Sample Holder and Cryostat System for the Low Temperature Measurements

campus of the State University of New York at Buffalo. Specimens were enclosed in an aluminum container and exposed to neutron flux for 2 hr. at the outer side of the reactor core. The total dose of fast neutrons was estimated to be not more than  $10^{14}$  nvt which is very small in comparison to irradiation doses used by other investigators. Annealing of these irradiated specimens as well as all the heat treatments of various samples to temperatures up to  $3000^{\circ}\text{C}$  were made in a graphite tube resistance furnace under nitrogen gas flow.

### C. Strain Amplitude Dependence

Curves of the dependence of internal friction  $Q^{-1}$  and of the dynamic elastic modulus  $E$  of polycrystalline graphite and baked carbon specimens on the strain amplitude were reported previously (Part IV, Fig. 12 and 13)<sup>4</sup>. They are reproduced here for convenience as Fig. 15 and 16. As was found previously  $Q^{-1}$  gradually decreases with decreasing amplitude towards a limiting value to be denoted by  $Q^{-1}$  while  $E$  is

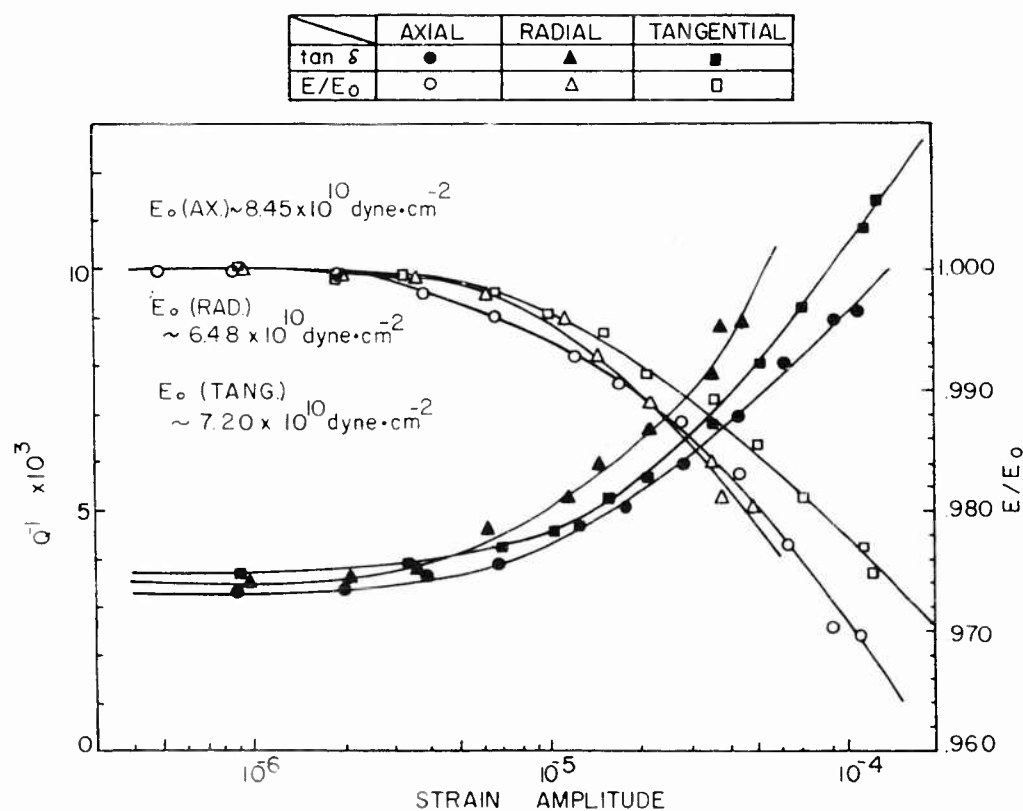


Fig. 15 Internal Friction and Dynamic Modulus of Polycrystalline Graphite as Functions of Strain Amplitude

	AXIAL	RADIAL
$\tan \delta$	●	▲
$E/E_0$	○	△

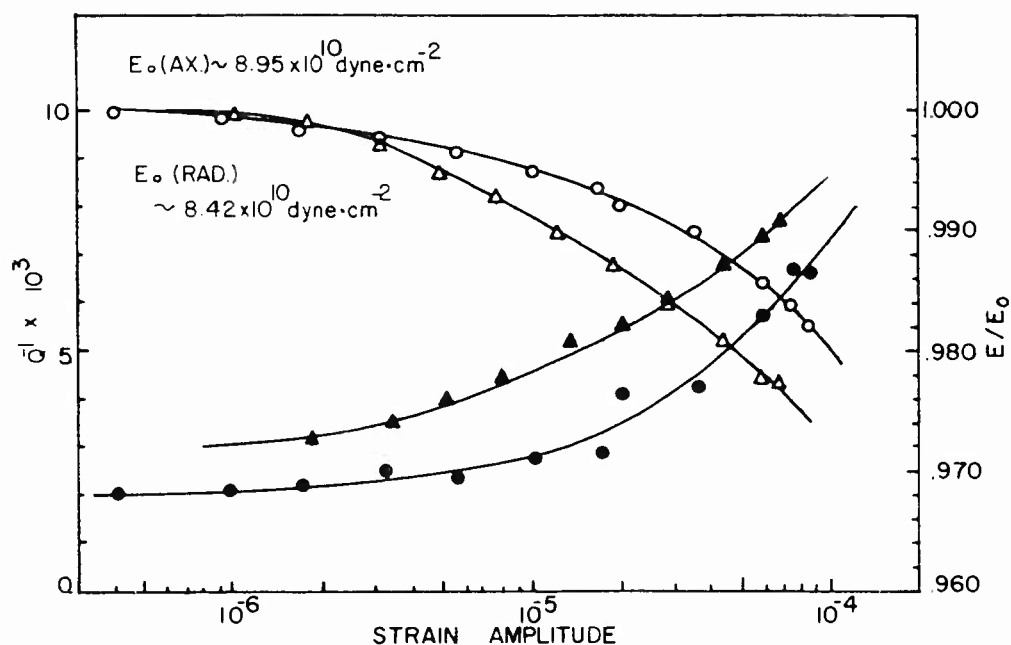


Fig. 16 Internal Friction and Dynamic Modulus of Baked Carbon as Functions of Strain Amplitude

found to increase asymptotically towards a constant value  $E_0$ . For a given material curves of  $Q^{-1}$  and  $E/E_0$  vs. strain amplitude begin to flatten out in about the same range of amplitudes. That is the internal friction as well as the dynamic modulus consist of two parts, an amplitude-dependent and an amplitude-independent part. As can be seen the amplitude-dependence parts equal to  $(Q^{-1} - Q_0^{-1})$  and  $(E_0 - E)/E_0$  are varying in parallel (linear relation) in agreement with the prediction of a theory of Granato and Lucke<sup>19</sup> concerning the mechanical damping caused by dislocations.

Results for glassy carbon are presented in Fig. 17. Although the internal friction of this specimen is extremely low with numerical values of the order of  $10^{-5}$  and the amplitude-independent region extends to higher strains than for the other conventional carbon products, the correspondence between variation of  $(Q^{-1} - Q_0^{-1})$  and  $(E_0 - E)/E_0$  is still holding well. That is the predictions of the theory of Granato and Lucke seem to be essentially in agreement with experiments even for an amorphous solid.

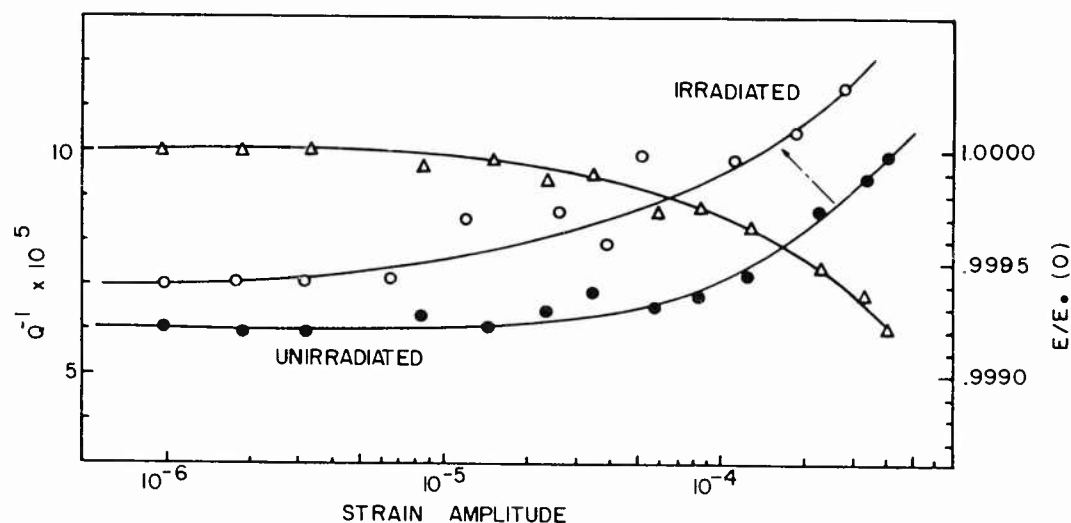


Fig. 17 Internal Friction and Dynamic Modulus of Glassy Amorphous Carbon as Function of Strain Amplitude Before and After Pile Irradiation

According to the Granato-Lucke theory the amplitude-dependent portion of internal friction is expressed in terms of a single function of the form

$$Q^{-1} - Q_0^{-1} = (C_1 / \mathcal{E}_0) \exp (-C_2 / \mathcal{E}_0) \quad (2)$$

where  $\mathcal{E}_0$  denotes the strain amplitude. Hence the experimental data plotted in the form of  $\mathcal{E}_0(Q^{-1} - Q_0^{-1})$  vs  $\mathcal{E}_0^{-1}$  should lie on a straight line which is sometimes called "Granato-Lucke plot." The corresponding results from our study are shown in Fig. 18. One can see that the theoretical relationship mentioned above is satisfied in good approximation for high amplitudes. Thus the mechanical energy loss even in poorly or little graphitized carbon solids is probably explainable in terms of the basic ideas of the Granato-Lucke theory, i.e., the loss being due to dynamical motion of glissile dislocations pinned down partially by point defects. It seems possible that even in such amorphous body as glassy carbon some dislocation-like patterns do exist and oscillate under alternating stress (although with an extremely small mobility).

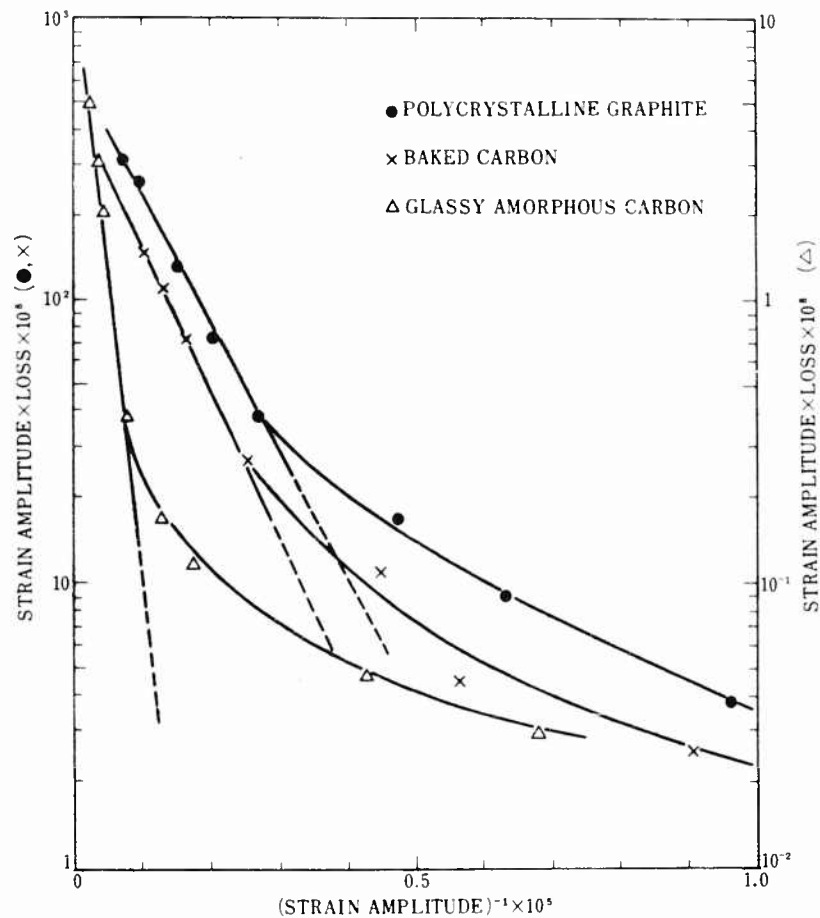


Fig. 18 Granato-Lueke Plot for Polycrystalline Graphite, Baked Carbon and Glassy Carbon

As easily seen the constants  $C_1$  and  $C_2$  in equation (2) correspond to the slope and intercept of the Granato-Lueke plot respectively. Taking into account various parameters connected with crystal imperfections these authors have given some structural meaning to these constants in their original paper. However because of the peculiar structure of graphite and carbons their assumptions (especially those concerned with the binding force between dislocations and the pinning point defects) are not applicable to our problem. In short, one has to modify the theory so as to make it applicable to the pinning mechanism of dislocations in carbon materials.

Finally, the results obtained for two pyrolytic graphites, the as-deposited at 2200°C and the 3700°C heat treated under tension are shown in Fig. 19. The as-deposited graphite gives quite small values of  $Q^{-1}$  and of  $(E_o - E)/E_o$  over the whole strain range examined. So far as the loss character is concerned, the as-deposited graphite in spite of the nearly parallel alignment of crystallites seems to be similar rather to the hard carbons than to the well-graphitized ones. Why the slight deviations from the ideal alignment known as "cone structure" should lower the mobility of dislocations so effectively would have to be clarified by special studies of this structure.

On the contrary, the 3700°C heat treated sample gives much higher values of  $Q^{-1}$  (by a factor of more than 10) and shows a remarkable amplitude dependence for both  $Q^{-1}$  and  $E$ . The extremely low value of electrical resistivity  $5 \times 10^{-5}$  ohm-cm indicates that all crystallites in this material are not only large and well developed but almost perfectly aligned parallel in one plane, although they probably are randomly oriented in relation to the c-axis. Thus of all carbon solids the loss character for this graphite should most closely approximate that of single crystals of graphite which possess the lowest concentration of structural irregularities impeding the motion of dislocations.

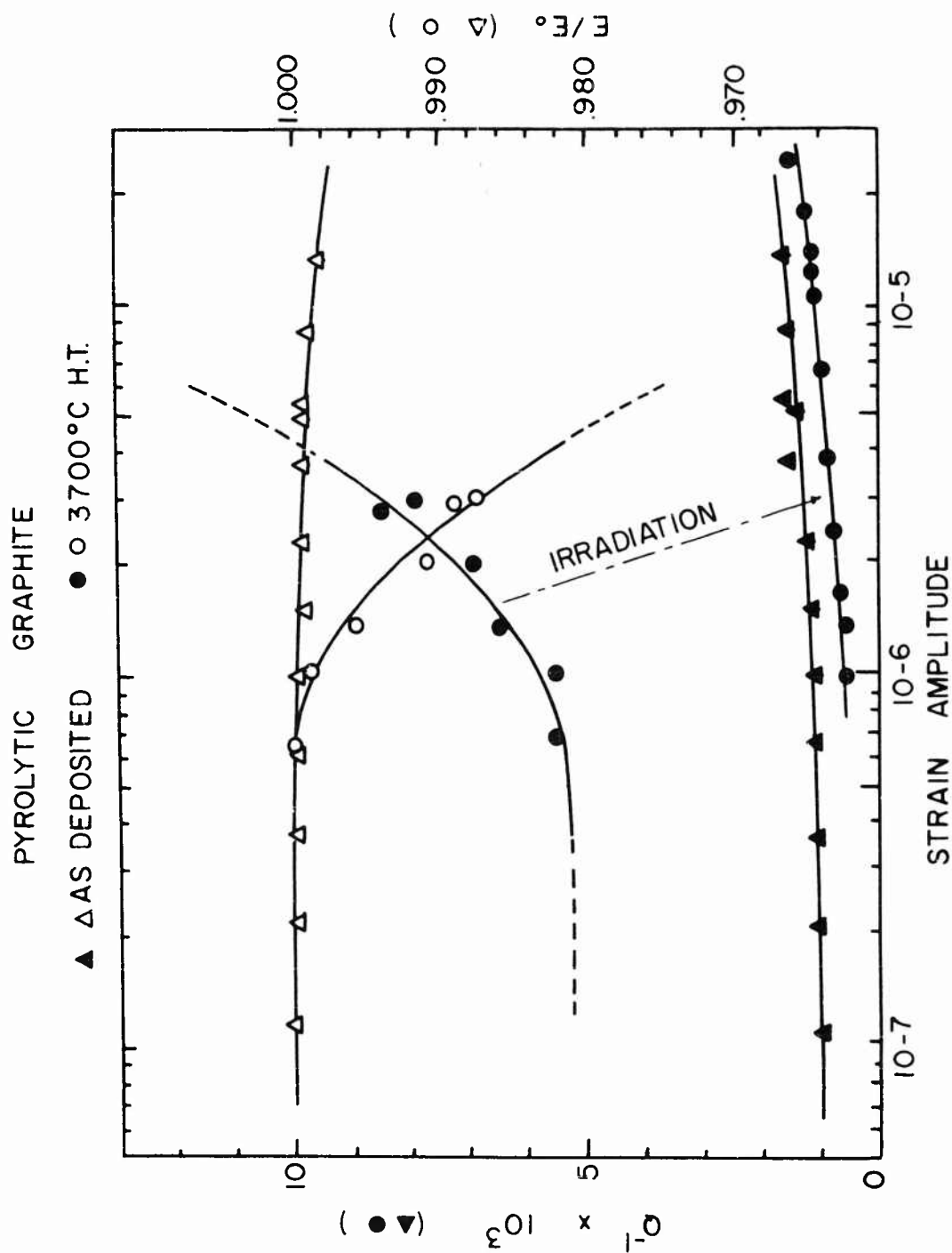


Fig. 19 Internal Friction and Dynamic Modulus as Functions of Strain Amplitude for As-Deposited Pyrolytic Graphite and for a Two-Dimensional Graphite (3700°C Heated Pyrolytic). Irradiation and Annealing Effects for the Latter are also Included

## D. Effect of Neutron Irradiation

### 1. Results

Fig. 20 shows examples of the internal friction vs. strain amplitude relationships obtained for a polycrystalline graphite before and after irradiation in the pile.

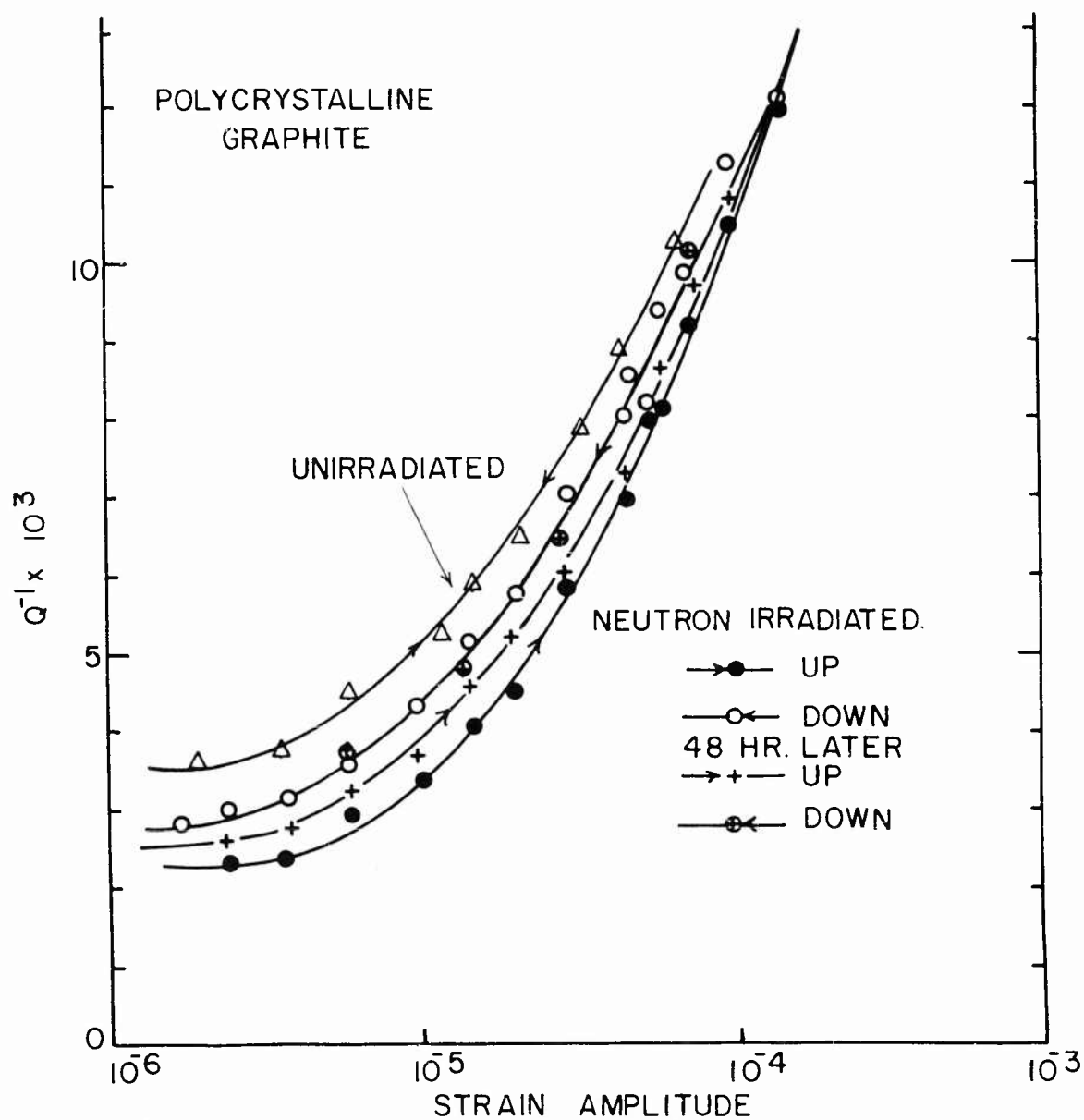


Fig. 20 Internal Friction vs. Strain Amplitude for Polycrystalline Graphite Showing the Influence of Neutron Irradiation

As mentioned before the total dose of fast neutrons was so small ( $\sim 10^{14}$  nvt) that no remarkable changes in the electric resistivity as well as in the external appearance were observed. Nevertheless, as a result of such slight irradiation the internal friction curve became measurably displaced. Moreover it exhibited hysteresis:  $Q^{-1}$  had somewhat higher values on the return trips when the amplitude was being decreased. Such an increase in  $Q^{-1}$  occurring as a result of vibrating the sample has been found to partly disappear after the specimen was left for a while to recover. A loop obtained 48 hr. later is also shown; the return part of the curve repeated the results obtained two days earlier.

It was found from the shift in the resonance frequency that after such weak irradiation the dynamic modulus increased by about 10 percent. A full recovery in both  $Q^{-1}$  and  $E$  was observed within the experimental accuracy when the specimen was annealed at  $3000^{\circ}\text{C}$ .

The effect of irradiation on the so-called two dimensional graphite is demonstrated in Fig. 21. One can see that slight irradiation causes a remarkable decrease in  $Q^{-1}$  down to about the same level the material exhibited before heat treatment to  $3700^{\circ}\text{C}$ . Hysteresis and recovery similar to those observed for the polycrystalline graphite were also found for this material as can be seen in Fig. 21. Again no change in the electric resistivity or in external appearance was observed after the irradiation.

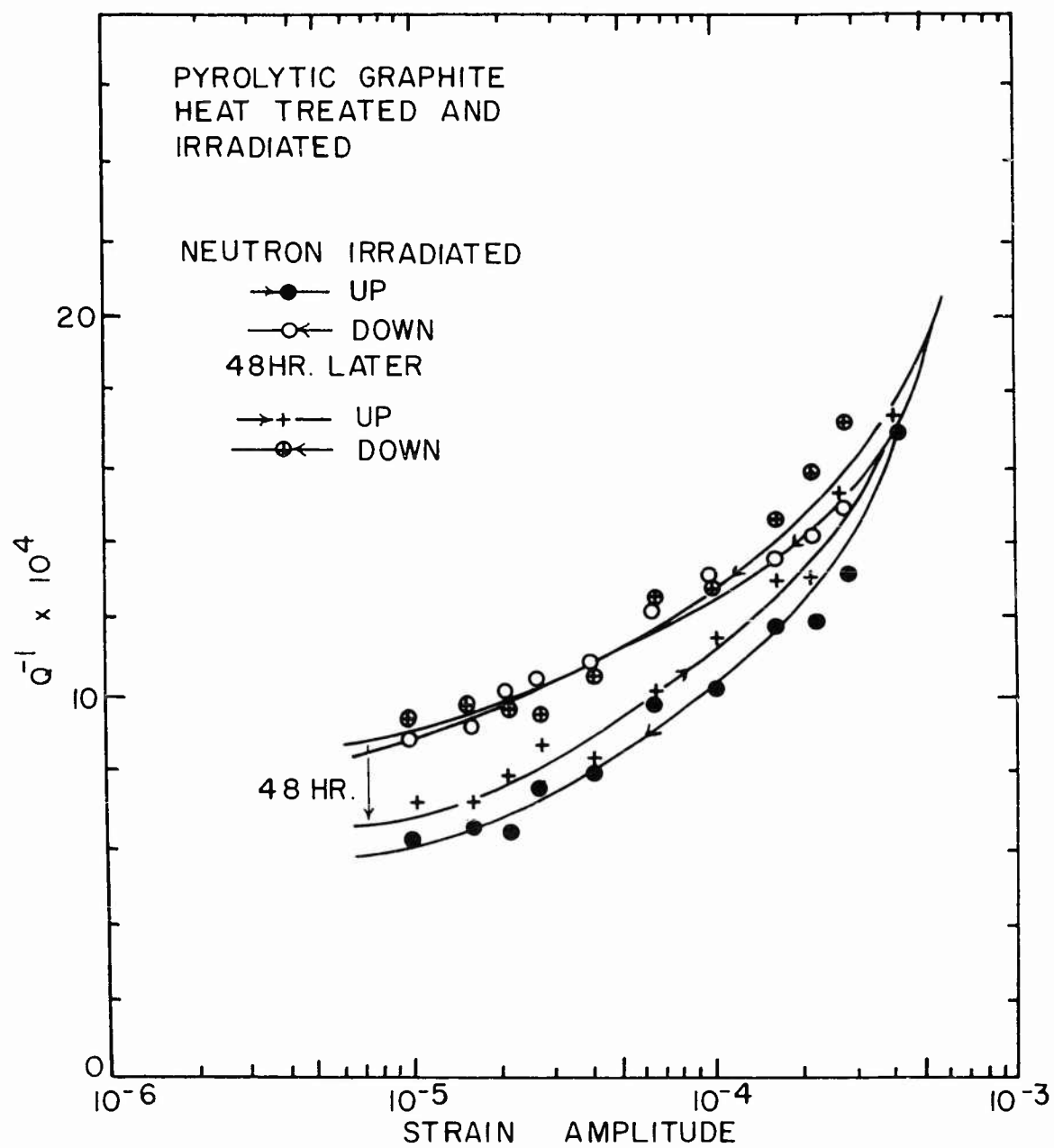


Fig. 21 Internal Friction vs. Strain Amplitude for a Two-Dimensional Graphite  
 Showing the Influence of Neutron Irradiation

The resonance frequency of the two dimensional graphite sample changed as a result of irradiation from about 2600 c/s to 6300 c/s; i.e.,  $E$  increased by a factor of about 6. This was very surprising since in general the elastic modulus of solids is known to be rather a structure-insensitive quantity. It is felt that this observation might be an important key for unravelling the nature of loss mechanism in the graphite structure.

The irradiated sample of two dimensional graphite was annealed at 3000°C (see Fig. 19). The internal friction increased remarkably after annealing but did not return completely to the original value observed before irradiation. As for the dynamic modulus it has recovered its original value as a result of this heat treatment.

The results for glassy carbon are presented in Fig. 17.  $Q^{-1}$  increases as a result of the irradiation contrary to the behavior of polycrystalline graphites. Hysteresis and partial recovery were not detectable in this case because of the extremely small values of  $Q^{-1}$ . No change in  $E$  due to irradiation was observed within experimental accuracy.

## 2. Discussion

The remarkable effects produced by irradiation and annealing are probably due correspondingly to the generation and to the elimination of point defects which participate in the pinning of dislocations. According to Seitz one fast neutron ( $\sim 1$  MeV) is expected to displace about 1000 carbon atoms in graphite lattice. Therefore the number of point defects produced by our irradiation ( $\sim 10^{14}$  nvt) should be of the order of  $10^{17}$  per  $\text{cm}^3$ , i.e., above  $10^{-4}$  atomic percent. Such a small number of defects which hardly can be detected even by the electron spin resonance causes no observable change in the electric resistivity as well as in other macroscopic properties. However the precipitation of these defects along the dislocation lines impedes the glide motion so effectively as to lower the internal friction. The length of dislocation strings limited by these pinning points is shortened by the irradiation possibly down to an order of  $100 \text{ \AA}$ .

For the irradiated two-dimensional graphite most of the knocked-on atoms are likely to recombine with vacancies on annealing at 3000°C, leaving a small number of most stable defects, e.g., atoms trapped at edge dislocations. Pinning of dislocations by such residual defects would be responsible for the incompleteness of the recovery of  $Q^{-1}$  by annealing shown in Fig. 19. It is remarkable that the presence of defects in concentration even much lower than  $10^{-4}$  atomic percent measurably affects the loss character.

Due to the remarkable anisotropy of graphite structure applied stress will exert a big shearing moment on the basal layers and as a result the basal dislocations will have a much higher mobility than in other crystals. Therefore, in the basic expression of strain  $\epsilon = \epsilon_{el} + \epsilon_{dis}$  where  $\epsilon_{el}$  and  $\epsilon_{dis}$  denote the strain components due to the pure elasticity and to the dislocation movement respectively. For graphite  $\epsilon_{dis}$  might be of comparable order of magnitude with  $\epsilon_{el}$  while for usual solids  $\epsilon_{el} > \epsilon_{dis}$  in the low strain range. One can easily see that this remark might also be important for explaining the behavior of  $Q^{-1}$  in connection with the pinning mechanism.

Two problems are left unexplained. The first are the hysteresis loops and recovery of  $Q^{-1}$  shown in Figs. 20 and 21. The partial recovery observed suggests the presence of a diffusion process. The second problem is the increase of  $Q^{-1}$  for

glassy carbon when the material is irradiated. For a completely amorphous body neutron irradiation might cause some structural relaxation rather than usual hardening. There is no point however to discuss these phenomena at the present time without having more information as to the nature of dislocations and point defects as well as their interactions in carbon materials.

#### E. Temperature Dependence

The temperature dependence of the amplitude-independent part of internal friction  $Q_0^{-1}$  and of the dynamic modulus (represented by the resonance frequency  $f$ ) was investigated for polycrystalline graphite for as-deposited pyrolytic graphite and for glassy carbon.

One can see from Fig. 22 that the curve of  $Q_0^{-1}$  vs. temperature for polycrystalline graphite possesses a remarkable peak at 50°K accompanied by a (sub-peak like) hump at 80°K. The corresponding curve of  $f$  vs. temperature (Fig. 23) exhibits a steep slope in the same temperature ranges as expected by the formal theory of anelasticity<sup>20</sup>. Substituting  $\omega = (2\pi f)^{-1}$  from the resonance condition and  $\tau_0 = 10^{-10} - 10^{-13}$  sec into equation (1) the activation energies are roughly obtained as follows:  $H = 0.07$  eV for the 50°K peak,  $H = 0.12$  eV for the 80°K peak. In analogy to similar peaks found for metals by a number of authors<sup>21, 22</sup> these two peaks are concluded to be the so-called Bordoni peaks for graphite connected with relaxation of the elementary motion of dislocations. The two values of  $H$  represent then the heights of the Peierls hills for the two types of basal dislocations which might be for instance the screw and edge components.

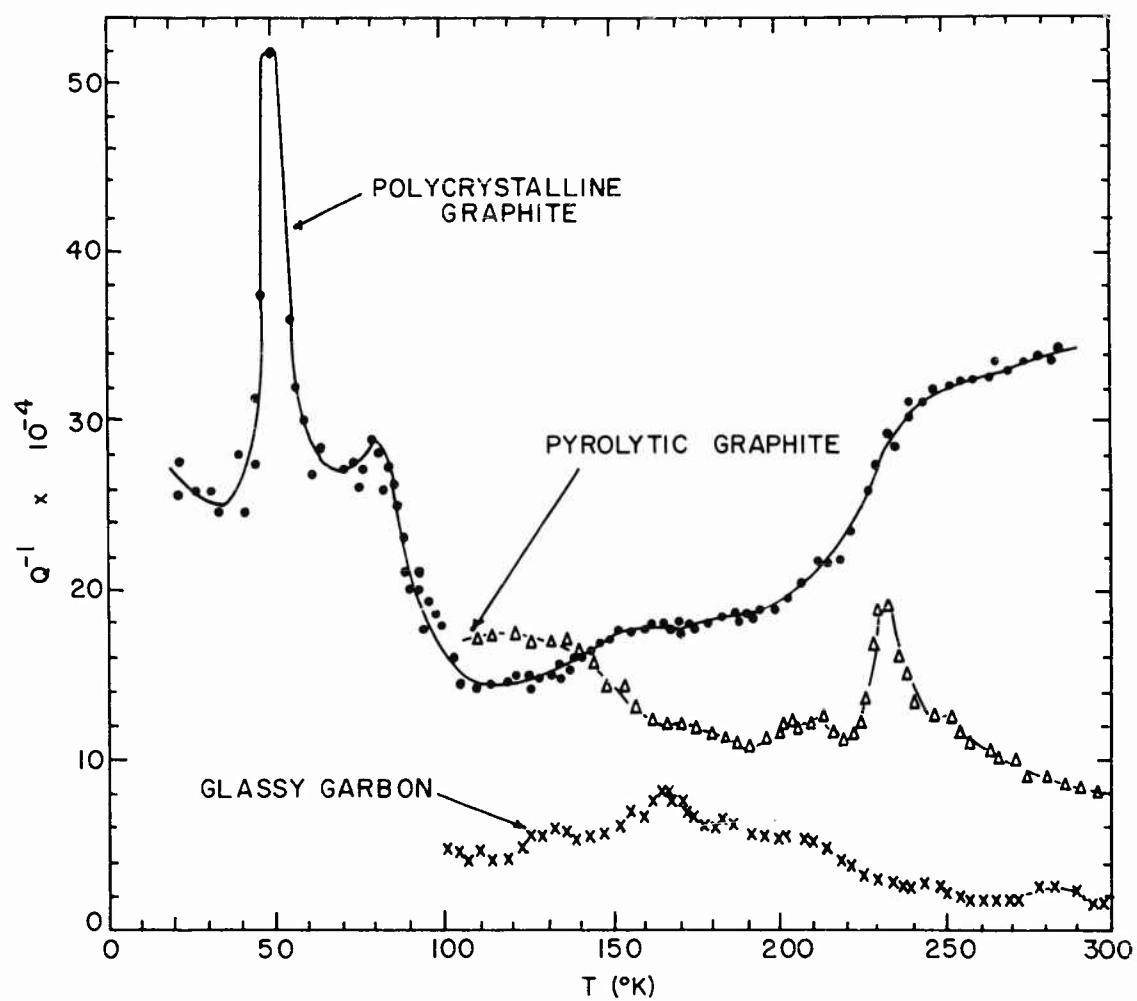


Fig. 22 Temperature Dependence of Internal Friction for Polycrystalline Graphite, Pyrolytic Graphite (As Deposited and Glassy Carbon)

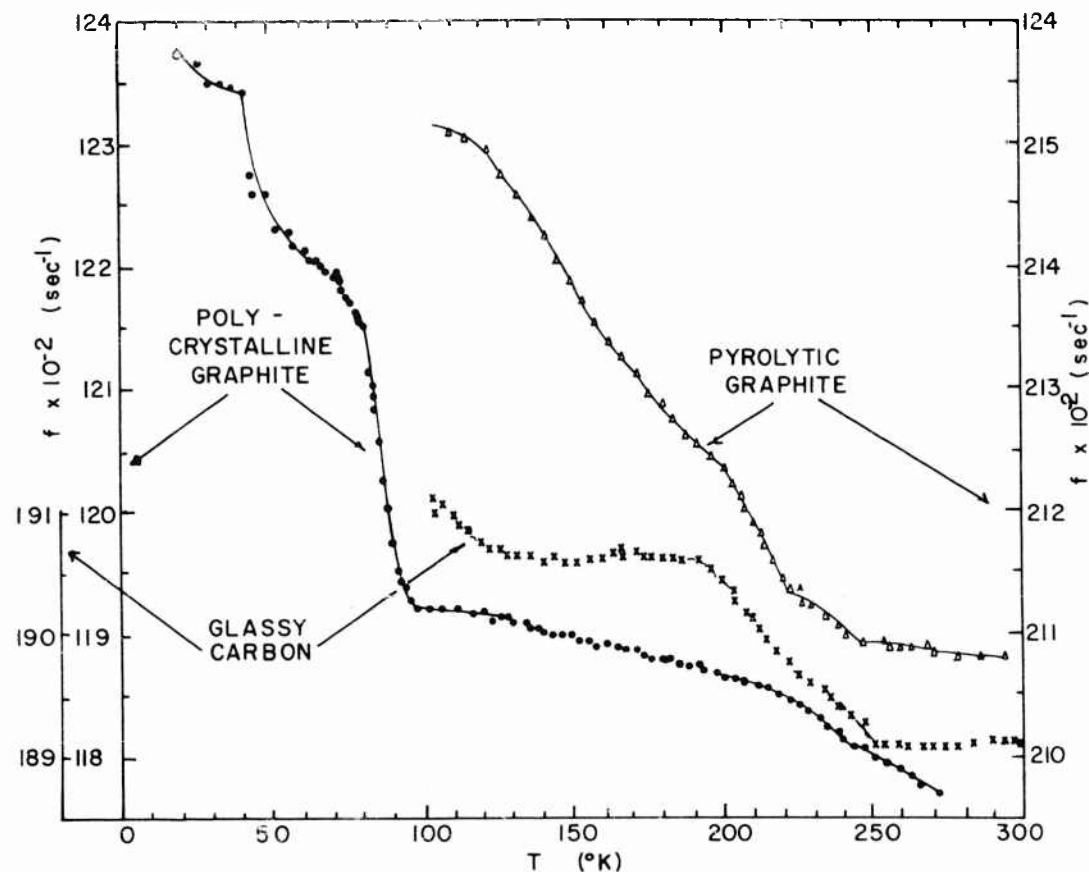


Fig. 23 Temperature Dependence of the Resonance Frequency for Poly-crystalline Graphite, Pyrolytic Graphite (As Deposited) and Glassy Carbon)

In the temperature range above 100°K no structure common to both diagrams in Fig. 22 and 23 was observed. The negative gradient of the curve  $f$  vs. temperature shown in the lower diagram is opposite to the well-known behavior of the elastic modulus at high temperatures but agrees well with the presence of the minimum of  $E$  at 200-300°C found by Mason and Knibbs<sup>23</sup>.

The pyrolytic graphite specimen gives in  $Q^{-1}$  a fairly sharp peak around 235° and a very small hump around 205°K. In view of lack of correspondence with changes in the modulus the bigger peak seems to be a "ghost peak" originating from the instrument but the smaller one seems to be rather intrinsic.

The glassy carbon shows three small humps at 135, 165 and about 200°K but no corresponding changes in the modulus are observed within the experimental accuracy. For such hard specimens with low internal friction as glassy carbon it will be advan-

tageous to improve the experimental technique by using rather the transversal vibration than the longitudinal. In general, it looks very worthwhile to extend the study for all carbons down to at least liquid hydrogen temperature.

#### F. Concluding Remarks

Summing up the results of this work one can say the following: 1) the dependence of the mechanical energy loss on strain amplitude as observed for various graphite and carbon materials agrees with the predictions of the theory of Granato and Lueke, the loss mechanism being mainly due to the dynamical motion of the basal dislocations pinned down by point defects, 2) the completely structureless glassy carbon behaves similarly to graphite, although the particular values of parameters are considerably different. Some dislocation-like patterns seem to exist in such an amorphous body, 3) slight neutron irradiation ( $\sim 10^{14}$  nvt) gives rise to remarkable changes in the loss character which can also be explained in terms of dislocations in line with the basic ideas of the Granato-Lueke theory, 4) the temperature dependence of internal friction for polycrystalline graphite exhibits two peaks at low temperatures, these peaks probably being the Bordoni peaks of graphite. The heights of the corresponding Peierls hills are roughly evaluated to be about 0.07 and 0.12 eV.

## V. THERMAL CONDUCTIVITY MEASUREMENTS

A detailed description of the apparatus designed and constructed and the technique used in making thermal conductivity measurements was given previously<sup>3, 4</sup>. The results obtained by tests conducted on many carbons have proved the reliability and accuracy obtainable with this improved design. Of particular interest was a series of tests made on soft filler-soft binder carbon material to determine the dependence of thermal conductivity and electrical resistivity on heat treatment (in the range 1000° - 2800°C) at various temperatures from 1000°C up to heat-treatment temperature. Corresponding preliminary results were presented in a previous report<sup>4</sup>. During the period of this report these investigations were extended and results were obtained also for the other three base carbon materials: soft filler-hard binder, hard filler-soft binder and hard filler-hard binder.

### A. Test Rod Data

All of the test rods made from the various carbon materials used were prepared in our laboratory. The calcined filler material was ground to proper size, mixed with binder and then extruded in the form of 1/2" dia. rods. The green rods were then baked to 1000°C in a baking furnace before heat treatment to various higher temperatures was initiated. Table III on the following page summarizes the materials and the mixtures used in the production of the test rods and also gives the apparent density after baking at 1000°C.

### B. Test Procedure to Determine Effect of Heat Treatment

The procedure followed for the series of runs to determine the effect of heat treatment was similar to that reported previously<sup>4</sup> for each of the four different types of carbons. For the carbon made from soft filler and hard binder, the baked rod was installed in the conductivity test chamber and the 2" helical heating coil was used as the heating element to provide the desired heat treatment. After installation of the test rod, the chamber was evacuated and charged with Argon gas at a pressure slightly greater than one atmosphere. This pressure was maintained throughout the series of test runs. As previously reported the insulation cylinder of Thermax powder was removed from the test chamber and was not used during these experiments. The rod was first heat treated to 1200°C by the heating coil and held for 10 min. at this temperature before being cooled to room temperature. The rod was then heated internally by applying voltage to the rod electrodes to produce the desired temperature for making measurements. At no time was the rod heated to temperatures above 1200°C (the heat-treatment temperature for the first series of runs). By varying the applied voltage the rod was heated to a desired temperature and data were obtained from which the thermal conductivity and electrical resistivity were calculated. The rod was then heated externally to a treatment temperature of 1500°C and the above procedure repeated with data obtained for temperatures up to 1500°C.

The heat treatment was increased in steps to temperatures of 1500, 1800, 2100, 2400 and 2800°C. After each heat treatment the thermal conductivity and electrical resistivity were determined for various temperatures from 1000°C up to the heat-treatment temperature. In order to achieve heat-treatment temperature above

Table III  
DATA ON 4 TYPES OF CARBONS  
Used for Thermal Conductivity Studies

	Soft Filler Soft Binder	Soft Filler Hard Binder	Hard Filler Soft Binder	Hard Filler Hard Binder
Filler	Soft Coke (Texas Coke)	Soft Filler (Texas Coke)	Hard Coke (Phenol Formaldehyde)	Hard Coke (Phenol Formaldehyde)
Binder	Soft Binder (M-30 Pitch)	Hard Binder (Phenol Benzaldehyde)	Soft Binder (M-30 Pitch)	Hard Binder (Phenol Benzaldehyde)
Filler Size	65/100 50 Parts ◀ 200 50 Parts	65/100 50 Parts 200/270 50 Parts	100/150 50 Parts ◀ 270 50 Parts	100/150 50 Parts ◀ 270 50 Parts
Filler Calcined Temp.	1200°C	1200°C	1200°C	1200°C
Binder Content	40 Parts	35 Parts	48 Parts	43 Parts
Mixing Temp.	140°C	127°C	140°C	140°C
Mixing Time	40 min.	15 min.	40 min.	15 min.
Density Baked (1000°C H. T.)	1.55	1.56	1.14	1.22

1800°C it was found necessary to apply power to the test rod in addition to the heating coil. This produced a radial temperature gradient in the test rod during the heat treatment. This gradient was much smaller than that maintained during the test runs and therefore probably had little or no effect on the test results.

In order to eliminate all temperature gradients during heat treatment the heat treatment part of the above procedure was changed for the investigation of soft filler-soft binder, hard filler-soft binder and hard filler-hard binder carbons. The heat treatment of these carbons was performed in a separate graphitizing furnace. The particular rod under test was removed from the test chamber after each series of runs for a given heat treatment and heat treated in the furnace to the desired next higher temperature level. The rod was then reinstalled in the test chamber and heated internally to produce the desired temperature for making measurements. Utilizing this technique the rods made from the different carbons given above were heat treated to temperatures of 1200, 1500, 1800, 2100, 2400 and 2800°C and data were obtained at temperature up to the heat-treatment temperature.

### C. Effect of Heat Treatment on Thermal Conductivity

The results showing the effect of heat treatment on the thermal conductivity obtained on the four different types of carbons are shown in Fig. 24, 25, 26 and 27. The results presented are the values obtained by actual measurement of a particular rod and no attempt was made to correct the various rods for density variation from one carbon to another. The broken curves show the changes that occur in the baked carbon as it is heat treated up to 2800°C.

Conductivity vs. temperature curves for carbons made using the soft filler (Fig. 24, 25) are very similar. In comparison the carbons made from hard carbon fillers (Fig. 26, 27) show a visibly different behavior, thus indicating the predominant part played by the filler material in the thermal conductivity.

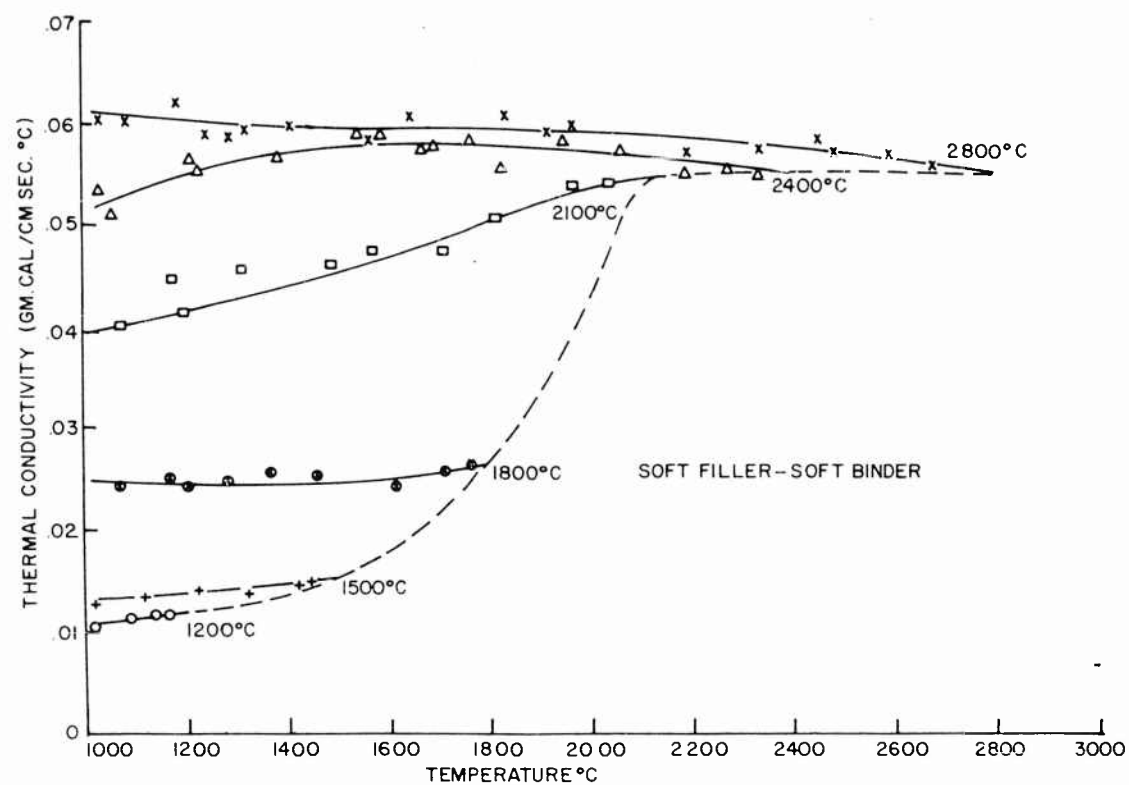


Fig. 24 Thermal Conductivity vs. Temperature for Various Heat Treatments of Carbons Made from Soft Filler and Soft Binder Carbon

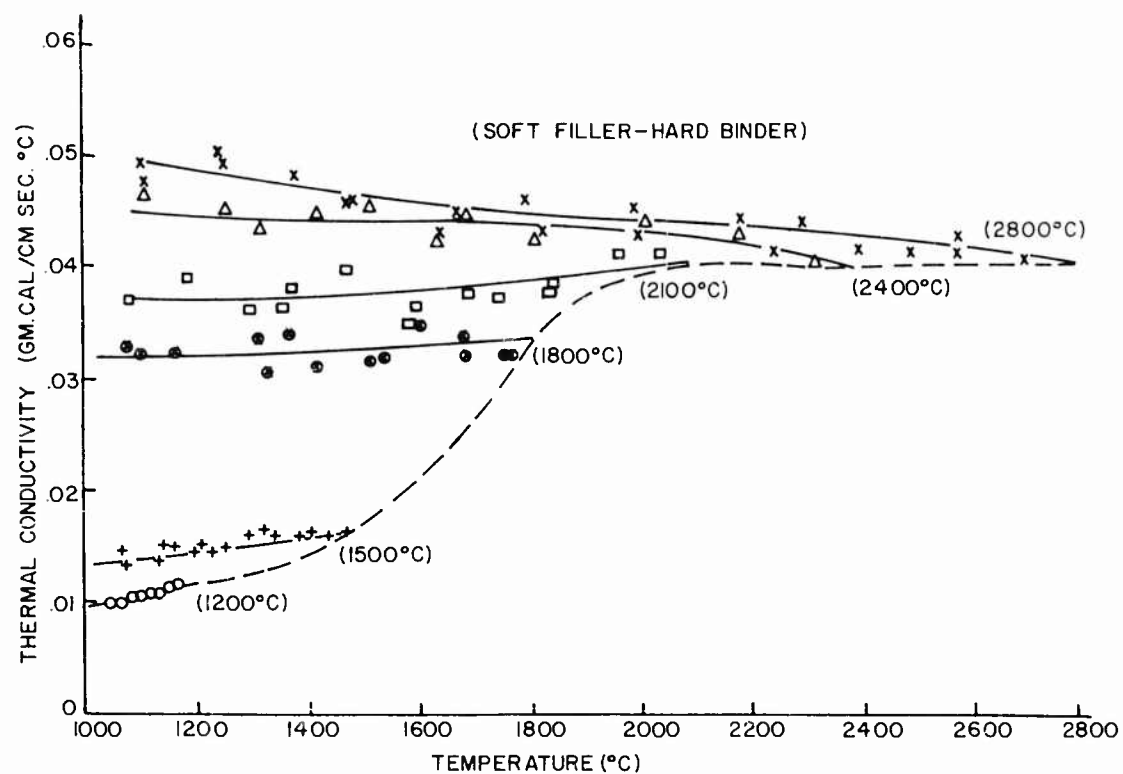


Fig. 25 Thermal Conductivity vs. Temperature for Various Heat Treatments of Carbons Made from Soft Filler and Hard Binder Carbon

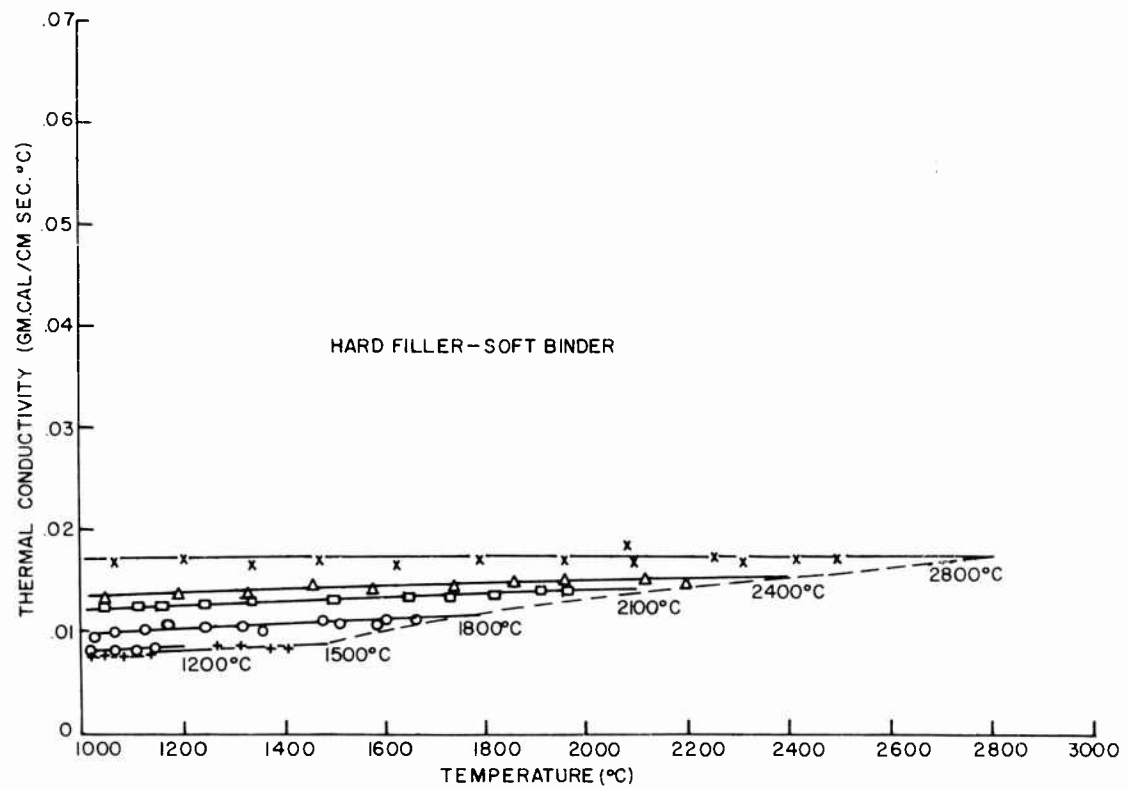


Fig. 26 Thermal Conductivity vs. Temperature for Various Heat Treatments of Carbons Made from Hard Filler and Soft Binder Carbon

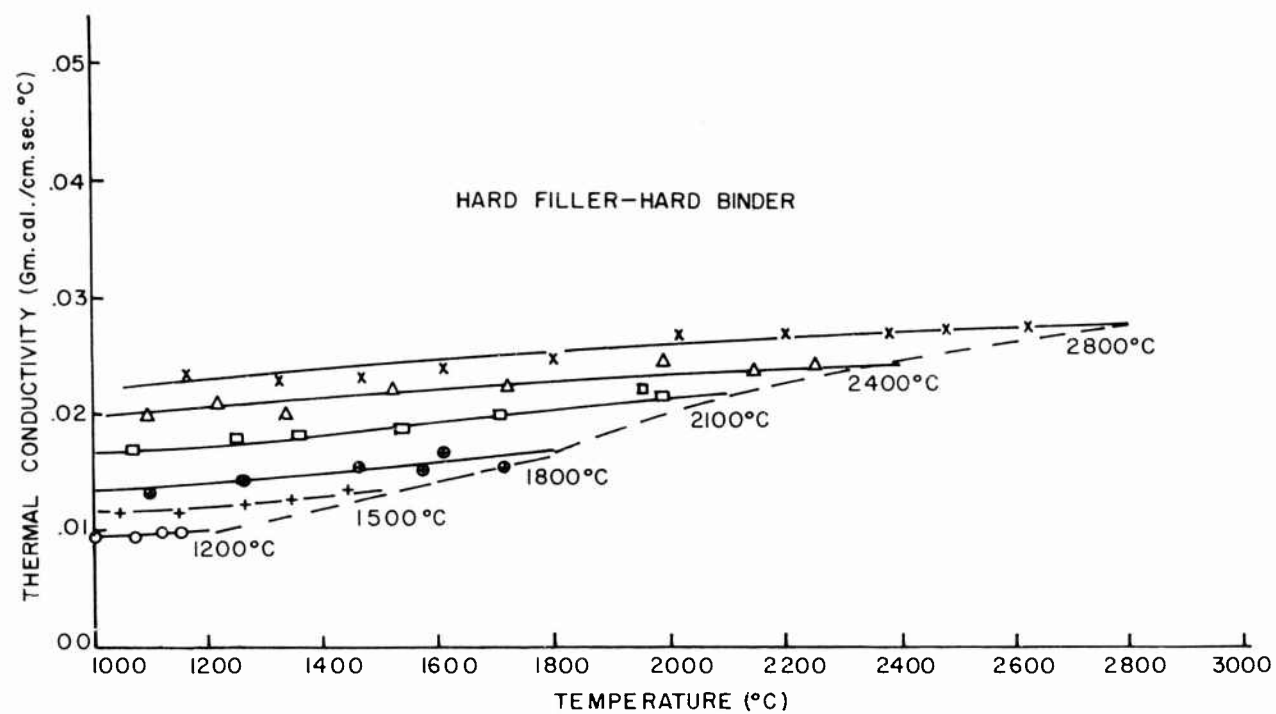


Fig. 27 Thermal Conductivity vs. Temperature for Various Heat Treatments of Carbons Made from Hard Filler and Hard Binder Carbon

In particular, the soft filler carbons show a positive temperature dependence of conductivity up to a heat treatment of about 2100°C but above 2400°C the conductivity shows negative dependence. On the other hand, the hard filler carbons show a positive dependence at all temperatures up to 2800°C although the hard filler-soft binder carbon appears to be temperature independent after heat treatment to 2800°C.

#### D. Effect of Heat Treatment on Electrical Resistivity

The effect of heat treatment on the electrical resistivity on the four different types of carbons is shown in Fig. 28, 29, 30, and 31. The resistivity was calculated from data obtained during the thermal conductivity measurement. There is a continuous decrease in resistivity with increase in heat-treatment temperature for all types of carbons.

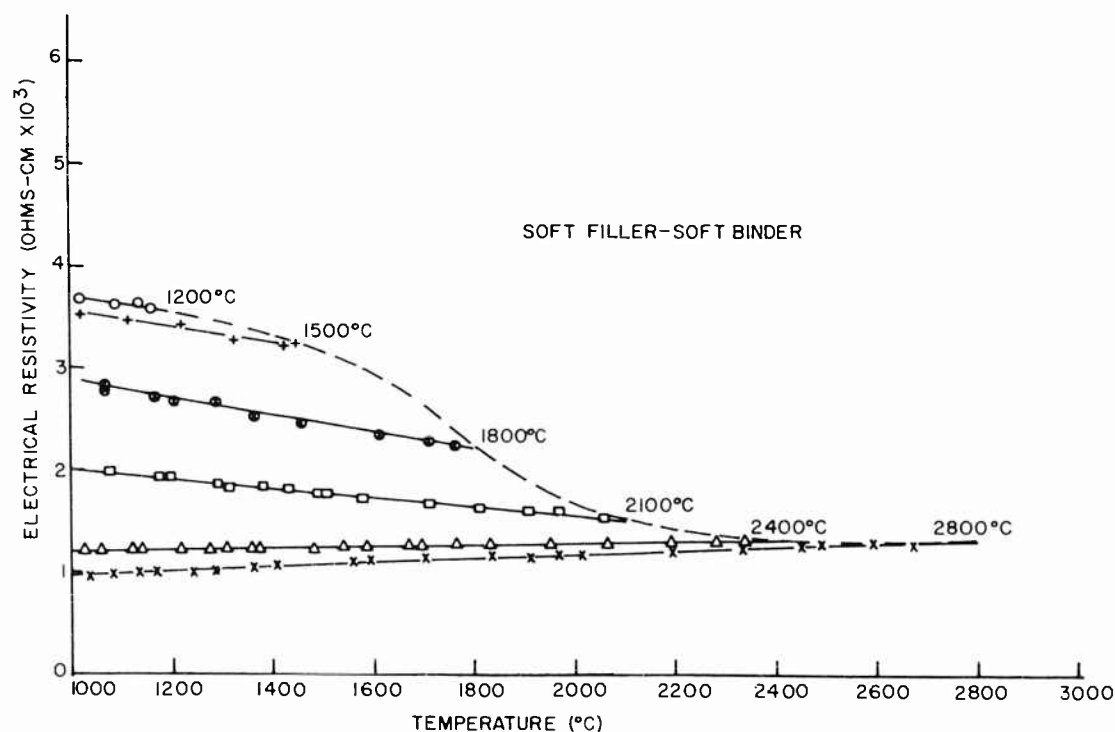


Fig. 28 Electrical Resistivity vs. Temperature for Various Heat Treatments of Carbons Made from Soft Filler and Soft Binder Carbon

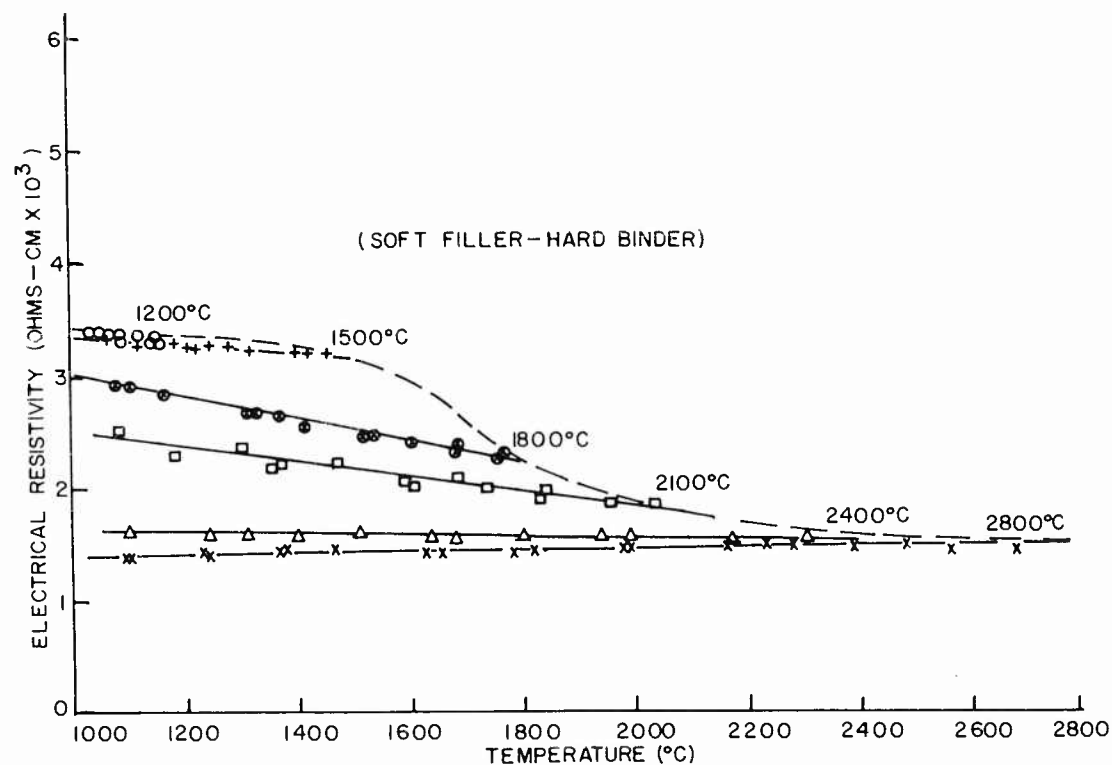


Fig. 29 Electrical Resistivity vs. Temperature for Various Heat Treatments of Carbons Made from Soft Filler and Hard Binder Carbon

Of particular interest is the temperature dependence of resistance for the carbons made from the soft filler carbons. For these carbons the resistivity shows negative dependence with temperature for heat treatment up to 2100°C. After heat treatment to 2400°C positive temperature dependence is indicated. The hard filler carbons show a negative temperature dependence for heat-treatment temperatures all through 2800°C. If temperature dependence is used as an indication of graphitization, it can be said that the soft filler carbons show graphitization for heat treatments above 2400°C whereas the hard filler carbons do not appear to have undergone any apparent degree of graphitization.

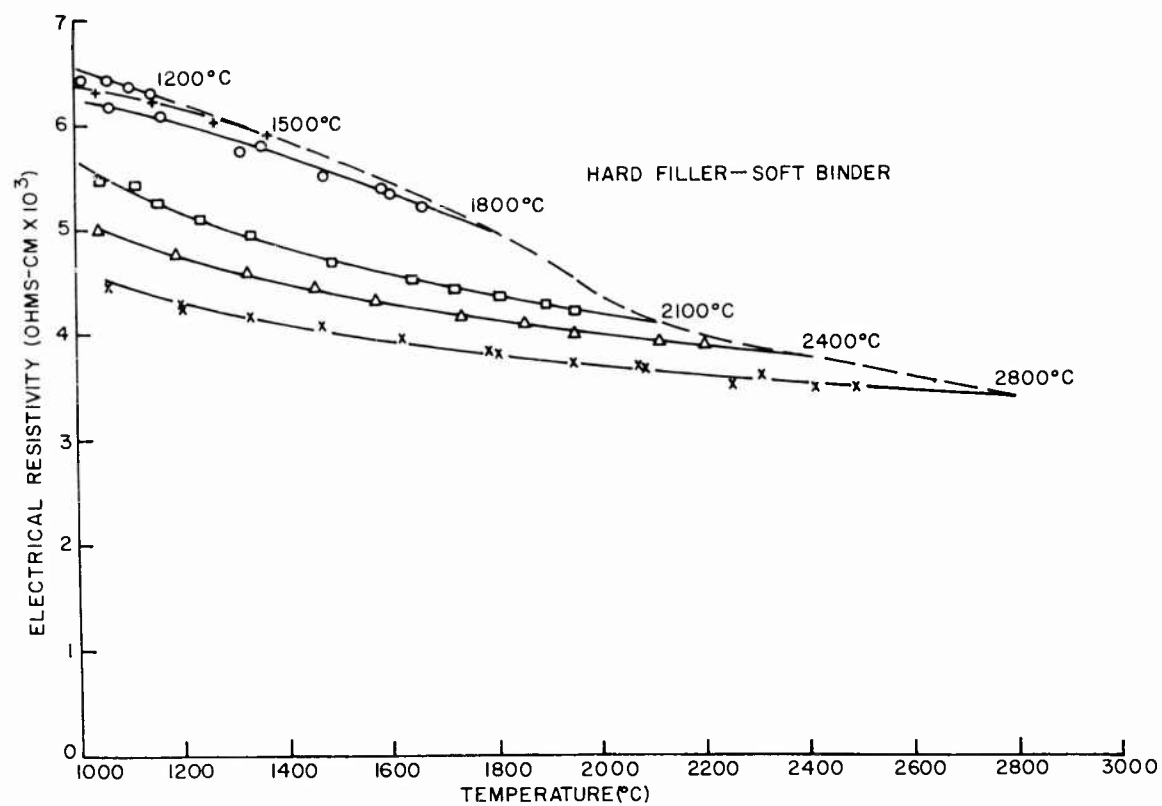


Fig. 30 Electrical Resistivity vs. Temperature for Various Heat Treatments of Carbons Made from Hard Filler and Soft Binder Carbon

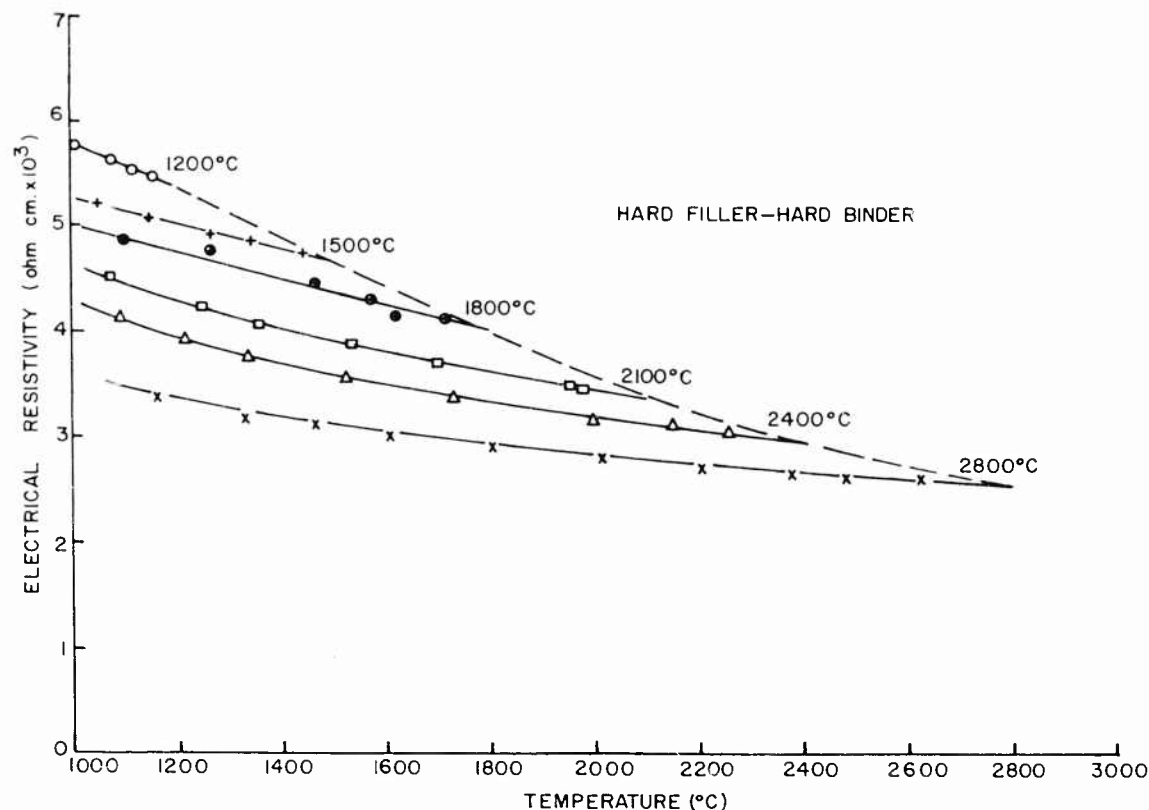


Fig. 31 Electrical Resistivity vs. Temperature for Various Heat Treatments of Carbons Made from Hard Filler and Hard Binder Carbon

#### E. Conclusions

The results of these measurements is the establishment of complete series of curves showing the effect of heat treatment on the thermal conductivity and electrical resistivity of carbons at various temperatures in the range of 1000° - 2800°C. This information is presented for carbons made from soft fillers and binders and hard fillers and binders.

The strong influence of the filler can be readily seen from a comparison of these results with the binder playing a secondary role. The effect of the hard carbon as either a filler or binder reduces the thermal conductivity and increases the electrical resistivity for a given heat treatment. The presence of hard carbons retards on the average the degree of graphitization during heat treatment.

There is no apparent correlation between the electrical resistivity and thermal conductivity. It can be seen that there is a wide range of thermal conductivity and electrical resistivity values and their temperature dependence. The factors that play an important role in determining these values are the carbon base material, the heat-treatment temperature and the operating temperature range.

## VI. THERMAL DIFFUSIVITY

### A. Introduction

A general description of the "steady" sinusoidal method has been previously given<sup>2,4</sup>. Theory, experimental technique and the rapid method of evaluation of the thermal diffusivity by using the data for the amplitude ratio  $A_{O1}$  and the phase shift  $\Delta\phi_{01}$  as obtained from the temperature curves recorded at the two longitudinally located points using a prepared chart were described in detail.

Using this technique some preliminary measurements were performed on copper and on stainless steel. The scattering of the results obtained was large and it was found that the deviation of the boundary conditions from the prescribed ones was mainly responsible for this scatter. The furnace and the apparatus were therefore further improved to produce more closely the prescribed boundary conditions and to extend the working temperature range up to 1200°C.

With this improved arrangement the thermal diffusivity of various graphites (heat-treatment temperature 2800°C) in the direction parallel to the extrusion axis was investigated throughout the temperature range 40-1200°C and a decrease in the scattering of the data was observed. The anisotropy of an extruded rod was studied by comparing the values of the thermal diffusivity in direction parallel and perpendicular to the extrusion axis as obtained respectively by the "steady" sinusoidal and "transient" methods throughout the temperature range where the two methods overlap.

### B. Preliminary Measurements

The preliminary measurements were performed by using the furnace and arrangement described in Part II<sup>2</sup>. Copper and stainless steel were selected, first because values of the thermal diffusivity for these materials are known and thus available for comparison and second, because it was important to determine the ability of the system to give correct results for a case of very large diffusivity (copper about 1.1 cm<sup>2</sup>/sec) as well as for a very small one (stainless steel about 0.04 cm<sup>2</sup>/sec). The ability of the experimental apparatus to be used for a wide range of thermal diffusivity is important because the variation of the thermal diffusivity with temperature in the range 0-1200°C is in general very strong for graphites, varying between the limits of diffusivity of copper and that of stainless steel. Fig. 32 shows the experimental values as well as the reference curves of the measured thermal diffusivity and of calculated  $K/\rho c$  vs. temperature taken from the literature for copper<sup>24</sup> and for stainless steel<sup>25</sup>. In general, the results showed that our system is able to operate for very large and very small values of the thermal diffusivity within a certain range of the reference values. However, the scattering was found to be large and caused by an erratic phase shift; the phase shift being in most cases either unreasonably large or low. An extensive analysis of the experimental conditions and of the recorded temperature waves was made in order to find the probable causes for such an unstable phase shift.

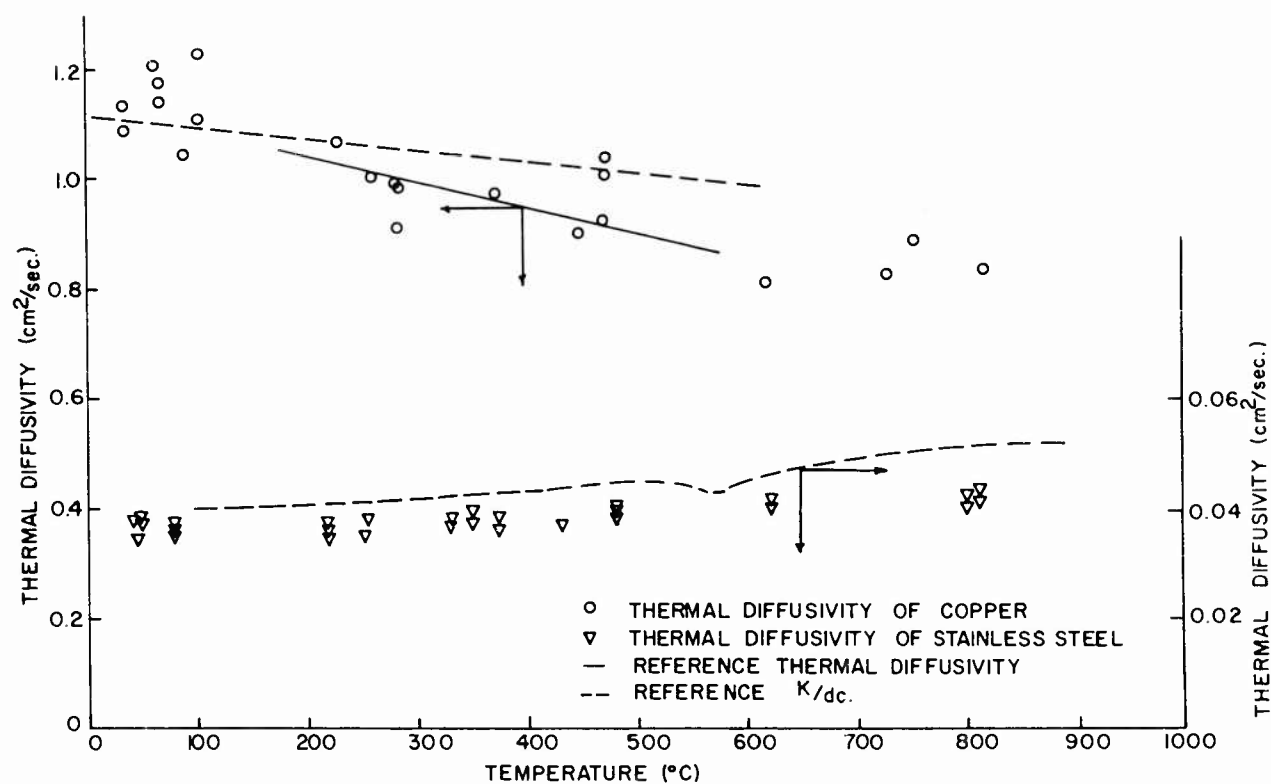


Fig. 32 Experimental Values of Thermal Diffusivity for Copper and Stainless Steel Compared With Published Values

The analysis showed that the phase shift is strongly dependent on variation in the time period, particularly if the phase shift is small as in the case of copper and, as found for stainless steel, on the non-uniform mean temperature distribution along the specimen. The furnace was therefore rebuilt and the apparatus modified in order to improve the above-mentioned conditions. Fig. 33 and 34 show respectively the new furnace and the experimental apparatus.

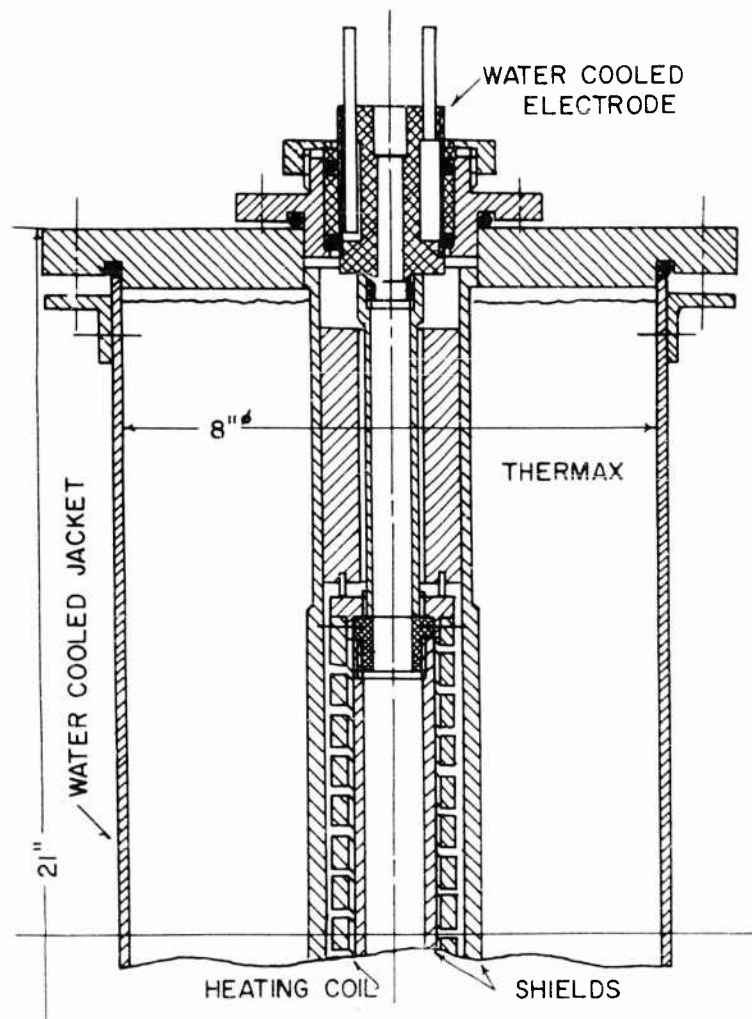


Fig. 33 Furnace for the "Steady" Sinusoidal Heat Flow Method

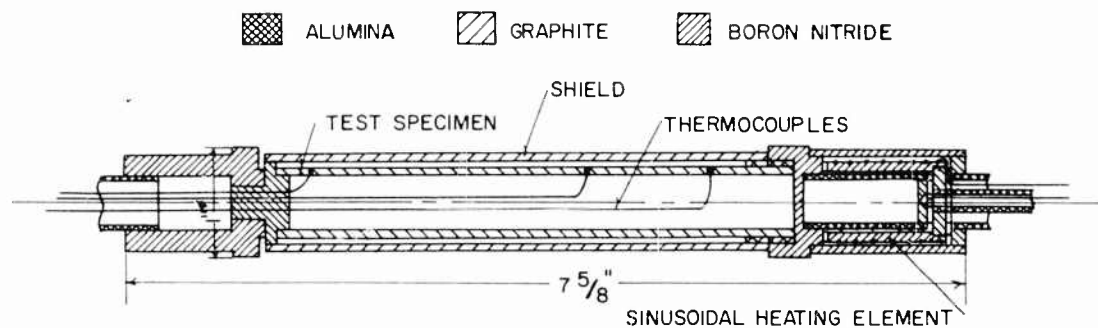


Fig. 34 Apparatus for Thermal Diffusivity Measurements

The wave form of the temperature variation was checked very closely and small deviations from a sinusoidal variation were found especially at the maxima as indicated on Fig. 35. Therefore a study of the power output of the sinusoidal voltage generator was undertaken. A plot of the power input to the heating element vs. time is shown in Fig. 36.

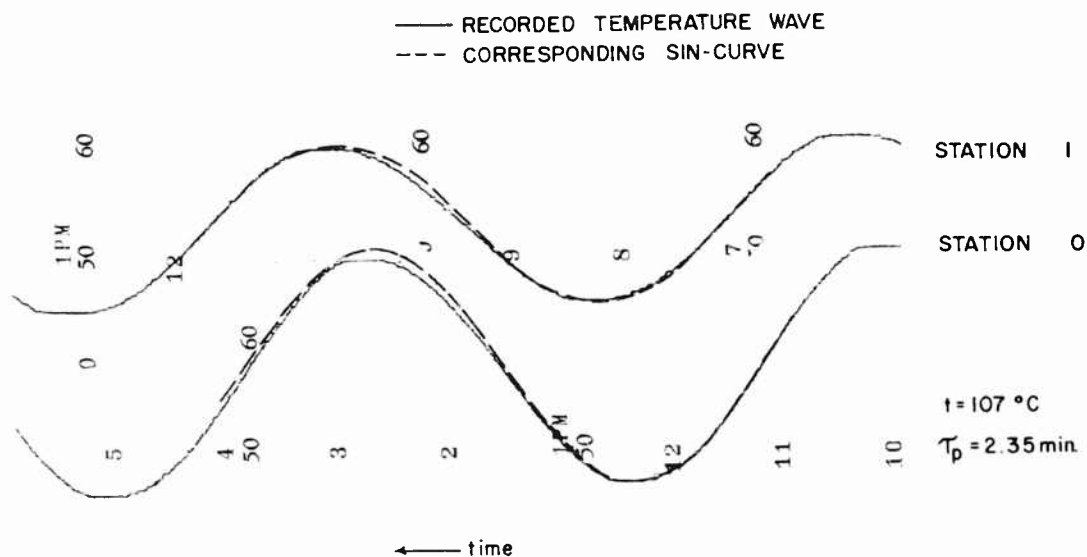


Fig. 35 Comparison Between Recorded Temperature Waves on Copper and Corresponding Sine Curves

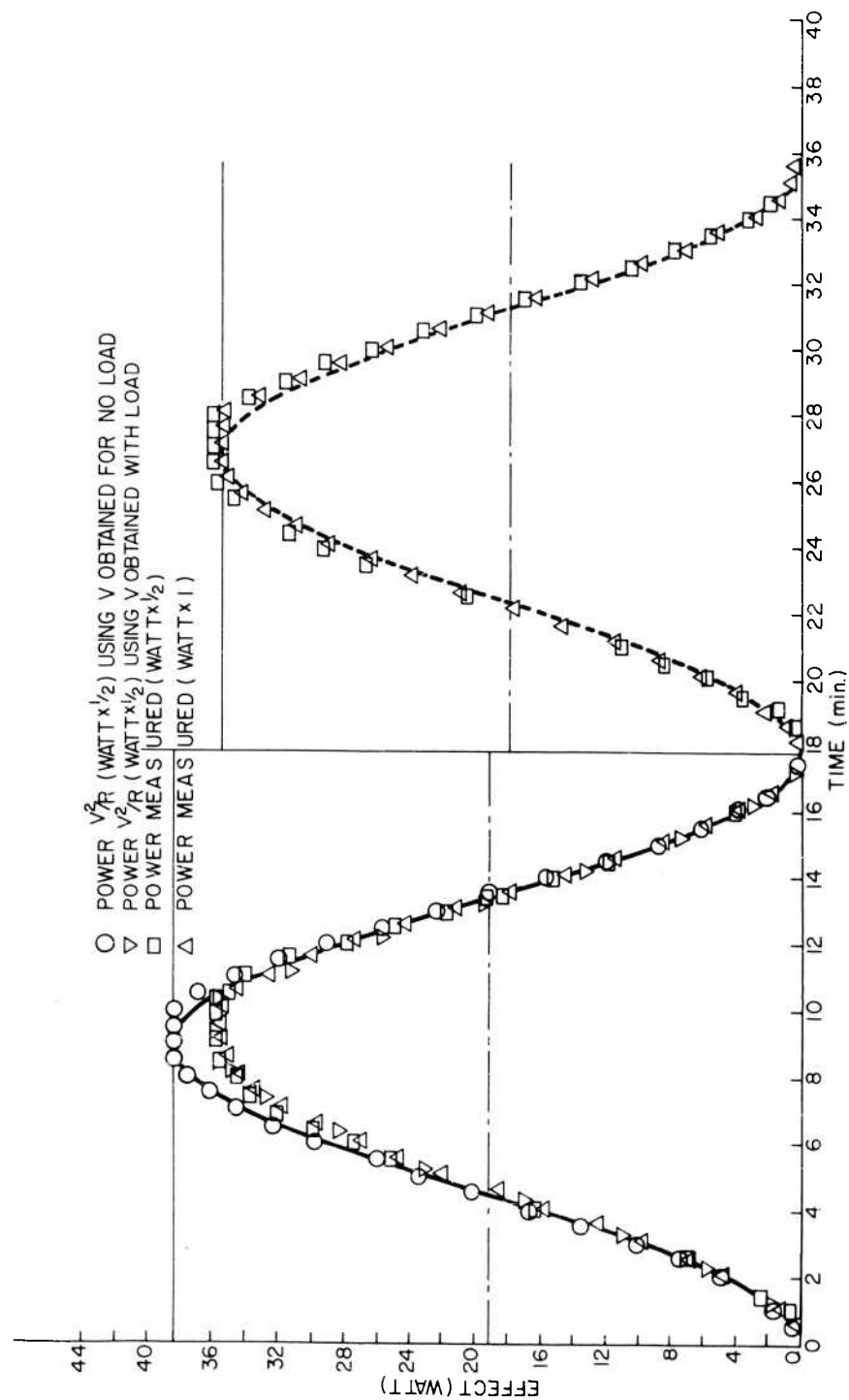


Fig. 36 The Power Input to the Heating Element vs. Time

The wave form deviates from the sinusoidal at the maxima; the shift of the curves to the right is due to the clearance in the scotch yoke. The hypothetical power curves for no load input to the heating element show a rather close agreement with the corresponding sine curve. However when load is applied the curves show some distortion in the region centered around the maximum power input. The distortion increases with increasing load and is primarily caused by contact resistances and losses in the variac and to a smaller degree by the increase in the resistance of the heating wire with temperature. Since the size of the deviation attributable to such distortion in the wave form is not known, to minimize the possible effect of this source of errors the efficiency of the heating element was increased, thus reducing the maximum power required; as a result the produced temperature waves were more closely sinusoidal.

### C. Results

Using the new arrangement measurements were performed on a number of typical carbons initially heat treated to 2800°C. Fig. 37 presents the curves of the dependence of thermal diffusivity parallel to the extrusion axis on temperature in the temperature range 40 - 1200°C. The two upper curves represent the diffusivity of two laboratory prepared soft filler-soft binder carbons "R" and "A" - the two lower ones are respectively for Thermax "W" and for laboratory made hard filler-hard binder carbon "Z."

A very strong temperature dependence of the thermal diffusivity is seen for the soft filler-soft binder carbons. At low temperature the thermal diffusivity of "R" is four times larger than for "Z" whereas at high temperature it is only twice as large. The hard carbon is less graphitizable and results are thus in agreement with expectations.

The scatter of the experimental data is small. A correct phase shift was obtained below 500° - 700°C; above this temperature the phase shift measured was found to be too small.

The mean temperature distribution along the specimen plotted for various temperatures is shown in Fig. 38. The mean temperature distribution deviates more and more from a uniform one as the temperature is increased. It appears that a temperature difference of more than 6°C between two stations causes a change in observed phase shift. This is perhaps not surprising because temperature amplitudes at the station O are of the same order, that is 5 - 12°C. Nevertheless, good results were obtained above 500° - 700°C because the effect of a faulty phase shift was minimized by selecting time periods which gave amplitude ratios within the range where the thermal diffusivity is independent of the phase shift.

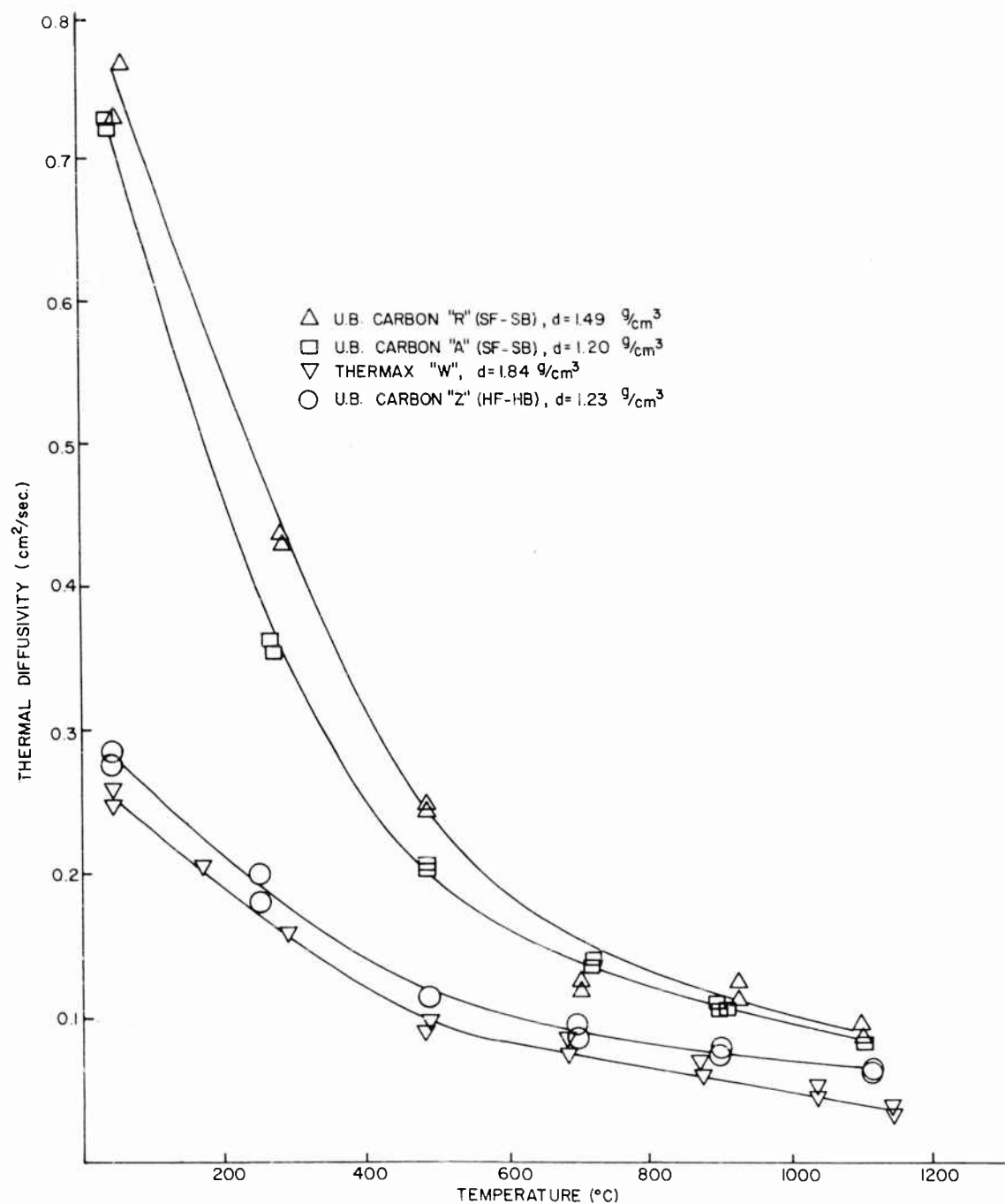


Fig. 37 Thermal Diffusivity Parallel to Extrusion Axis vs. Temperature for Various Carbons. (Heat-Treatment Temperature 2800°C)

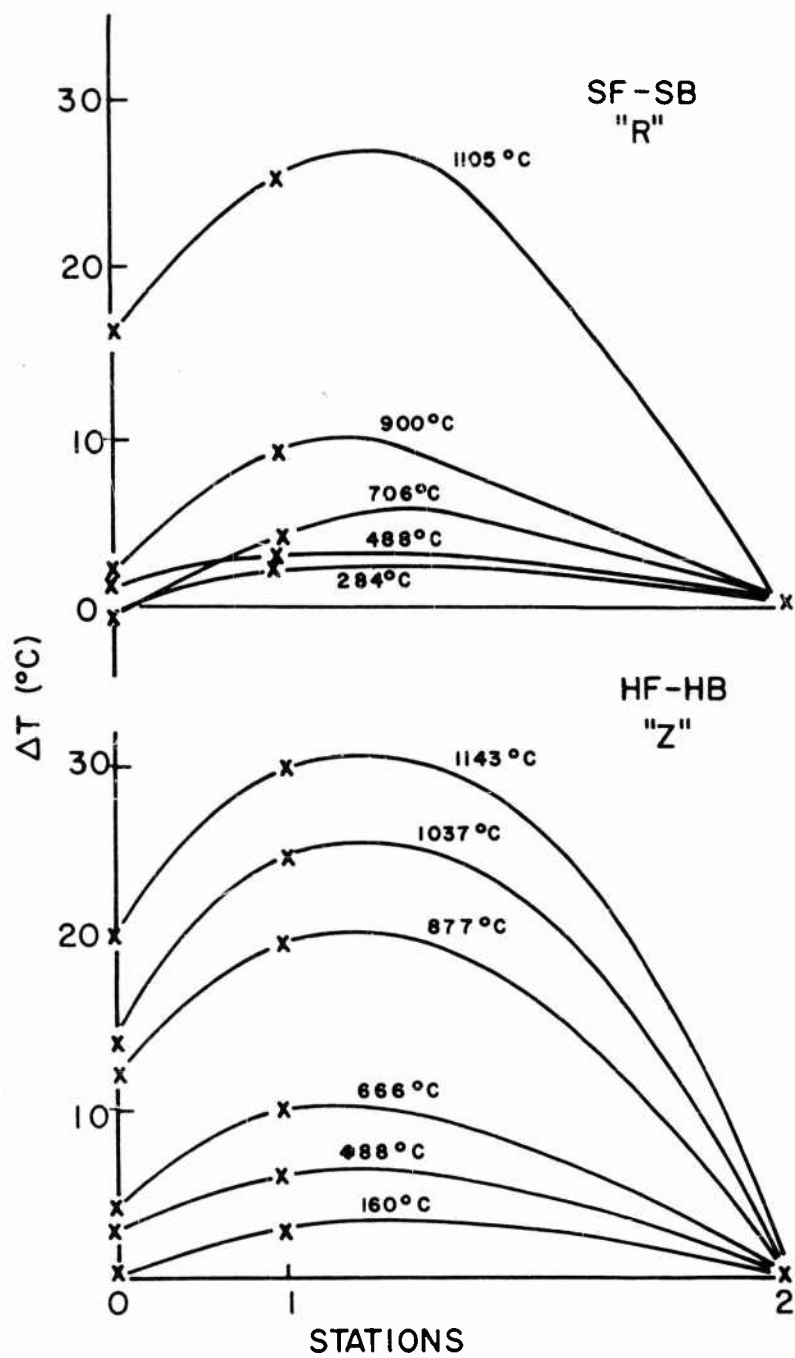


Fig. 38 Temperature Distribution Along Specimen in Reference to the Temperature at Station 2 (Insulated End)

Fig. 39 and 40 show the temperature dependence of the thermal diffusivity in the temperature range 40 - 2400°C by combining the results obtained by the sinusoidal and by the transient heat method. The two curves for each carbon do not overlap but show a shift in the temperature range where both techniques yield data. The shift indicates an anisotropy of the rods that is a difference between the direction parallel and perpendicular to the extrusion axis. This anisotropy would probably be even more pronounced if the specimens used in both methods had been made on 1/2" dia. extruded rods. However for practical reasons the specimens used in the steady "sinusoidal" technique were made from 1" dia. extruded rods with a smaller density.

#### D. Conclusions

The results show that the thermal diffusivity at relatively low temperature is mainly dependent on the crystallite size. Thus for carbons heat treated to 2800°C the thermal diffusivity is much larger for highly graphitized carbons (soft filler-soft binder) than for poorly graphitized carbons (hard filler-hard binder) at the same ambient temperature. The thermal diffusivity of a carbon is only slightly dependent on density, decreasing as the density is decreased. The extruded rods are in general more or less anisotropic.

Measurements of the thermal diffusivity employing the "steady" sinusoidal heat flow method are not easy and very time-consuming; for instance 6-12 hours are required to determine a single value of the thermal diffusivity. The experiments have shown that the method is extremely sensitive. This suggests that a high precision can be achieved if the prescribed initial and boundary conditions are sufficiently well satisfied. Despite all the difficulties encountered, the method has been developed to such a degree that when good care is exercised and proper time periods are selected good results are obtainable in the temperature range 40 - 1200°C.

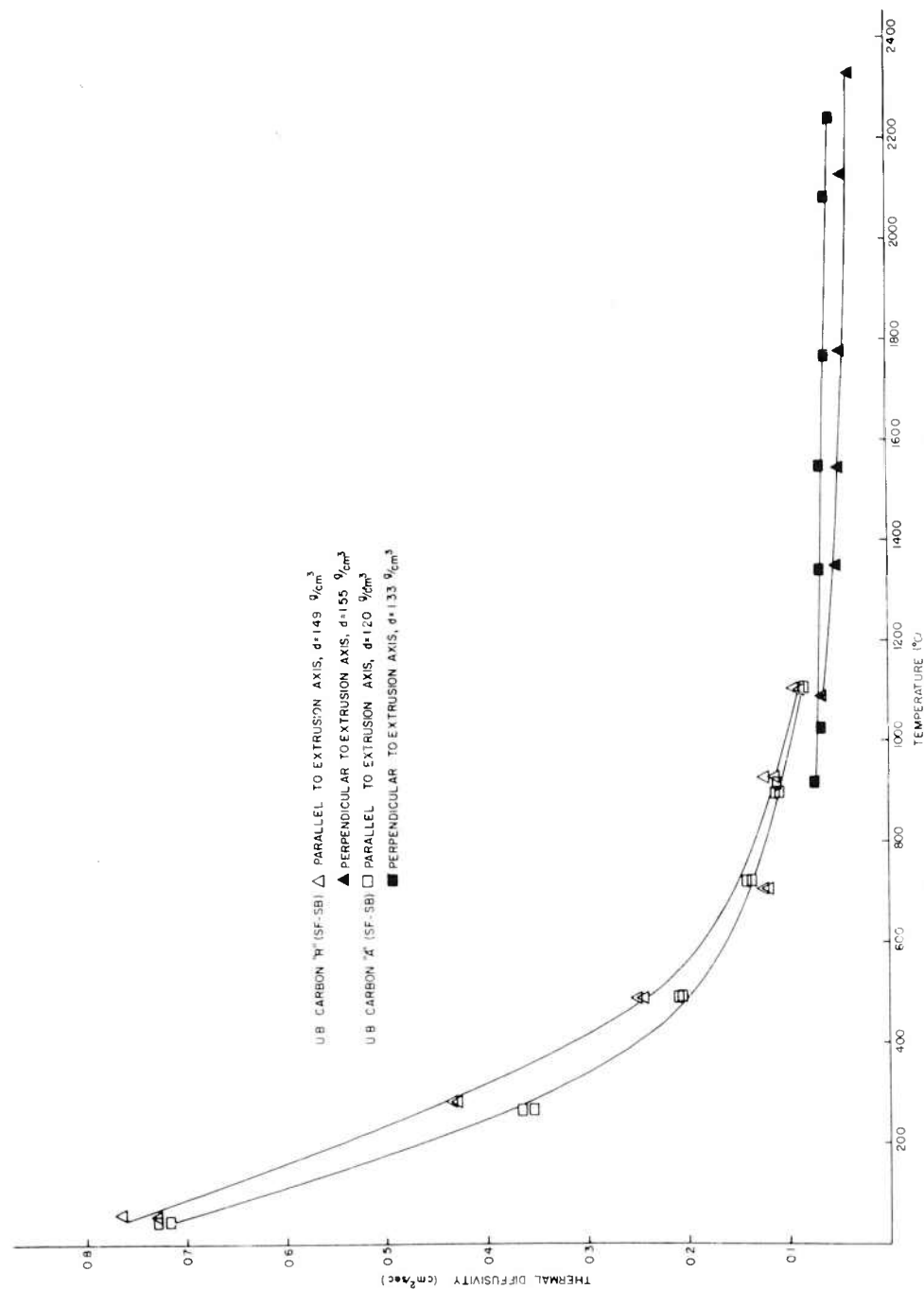


Fig. 39 Thermal Diffusivity vs. Temperature for Soft Filler-Soft Binder Carbons

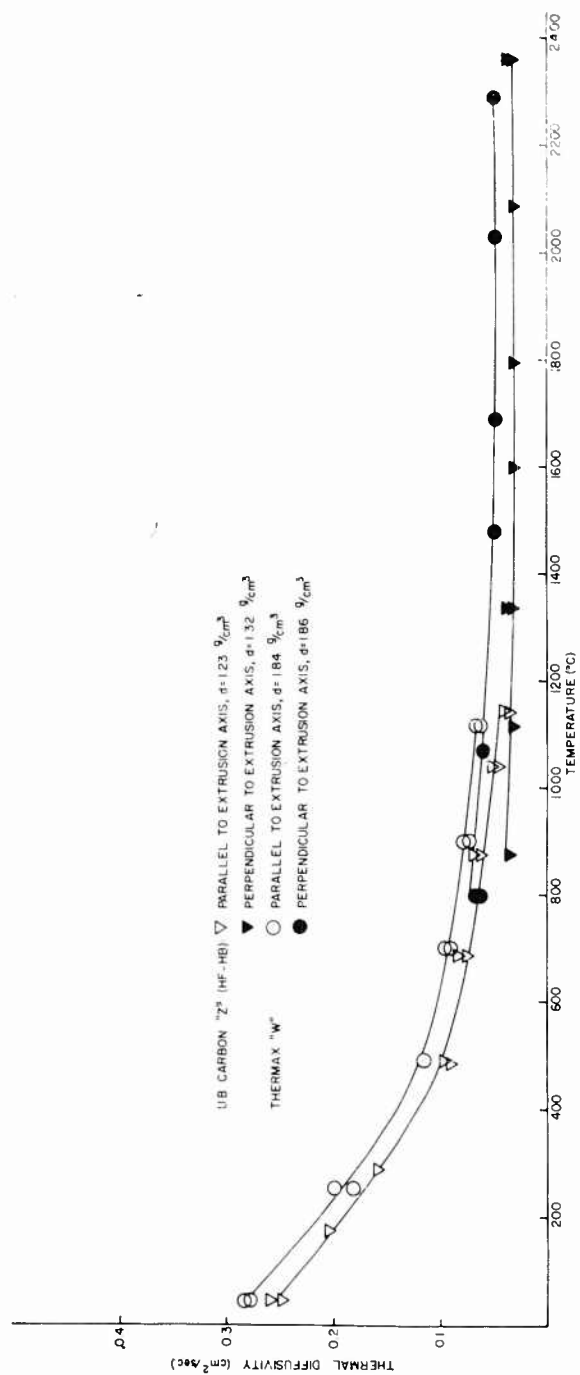


Fig. 40 Thermal Diffusivity vs. Temperature for Hard Filler-Hard Binder Carbons

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